STUDIES of MINERAL DEPOSITS

V. I. Smirnov, A. I. Ginzburg,
V. M. Grigoriev, G. F. Yakovlev

Studies of Mineral Deposits

BY V.I. SMIRNOV (Ed.), A.I. GINZBURG,
V.M. GRIGORIEV, G.F.YAKOVLEV

The purpose of this volume is to
introduce the student majoring in
geological aspects of mineral
deposits to industrial development
of ferrous and non-ferrous ore
deposits as well as the deposits
of rare earths, precious and radio-
active metals, and scattered
elements. For each metal and its
most important geological deposits
in the USSR and other countries,
the book presents data on its
historical and economical back-
ground and describes its geo-
chemistry, mineralogy, and metallo-
genic properties.

The book is intended as a college
text but will also be of interest to
industrial geologists.

STUDIES
of MINERAL
DEPOSITS

В. И. Смирнов, А. И. Гинзбург,
В. М. Григорьев, Г. Ф. Смирнов

Курс
рудных месторождений

Редактор
академик В. И. Смирнов

V.I. Smirnov (Editor), A.I. Ginzburg, V.M. Grigoriev, G.F. Yakovlev

STUDIES of MINERAL DEPOSITS

English translation edited by
Prof. A. A. BEUS, D. Sc. (Geol. and Min.)

Translated from the Russian by
A. Zilberman, Yu. Prizov, T. Lokhova

PREFACE

This book is intended for mining engineers and geologists as well as for under-graduate and postgraduate students engaged in the study of mineral deposits.

Since the general conditions of mineral deposits formation and their genetic classification are considered in a special course, the principal problems of the ore formation theory are not discussed in this book. However, some special problems of the ore formation theory are reviewed while dealing with the mineral deposits of individual metals.

The authors have described the mineral deposits in relevance to the main metal component. The description contains sections covering geology and genesis of ferrous, non-ferrous, rare, dispersed, noble and radioactive metals. Deposits of 56 individual metals and their associations are analyzed in the book.

The authors have sought to describe ore deposits of each individual metal or their natural combinations in keeping with a certain scheme. The description begins with an outline of historical and economic data, followed by geochemical and mineralogical characteristics of a given metal. Special attention is paid to the ways and means of metal concentration resulting from endogenous and exogenous processes in the Earth's crust. Metallogenic information is also given to characterize the origin and distribution of mineral deposits in relation to geosynclinal and platform stages of geo-logic history with due account of metallogenic epochs. Finally, commercial types of deposits are described on the basis of various representative examples.

The grouping of commercial types of ore deposits is based on a single genetic classification, i. e. on endogenous, exogenous and metamorphogenic series. The endo-genous series incorporates magmatic, pegmatite, feldspar metasomatite (albitites included), greisen, carbonatite, skarn, plutonogenic hydrothermal, volcanogenic hydro-thermal, massive sulfide and stratiform deposit groups. Within the exogenous series the following groups have been characterized: weathering, placers, sedimentary, mineralized waters and brines. The metamorphogenic series is subdivided into the metamorphozed and metamorphic groups. The groups are in turn subdivided into classes. Where the need for a more detailed description is in evidence the authors have differentiated ore formations within genetic classes as determined by similarity of mineral composition of ores and by the geologic environment of deposits.

At present about 20 000 real ore deposits have been discovered in the world. It is impossible to describe even a small fraction of that number of deposits in one single book. The authors have characterized the most representative examples of commercial types of ore deposits in the USSR and elsewhere. They have endeavoured to select such examples that could prove valuable for augmenting our knowledge about the most important mineral deposits of the world and for interpreting the geologic environment of their formation, exploration, prospecting and evaluation. First priority in selecting examples was given to deposits which were studied in detail irrespective of their development stage. The examples refer to both newly discovered deposits and

deposits being mined, as well as those which may have been largely exhausted. The depth of insight into the characteristics of deposits depends on how detailed information available is. Within the limited space of the book we have to follow a rigid pattern of concise presentation. For the same reason the book provides selected rather than complete bibliography.

This work is based on lectures read by the authors at the Moscow State University and the Moscow Institute of Geologic Exploration, and is supplemented with information based on their experience in the study of various ore formations.

They used the classic Russian literature on the subject: the courses on mineral deposits published by K. I. Bogdanovich (1913), M. A. Usov (1933) and V. A. Obruchev (1934), the second edition of *Ore Deposits of the USSR* (three volumes, 1978, in Russian), as well as the best known textbooks on the subject published in Europe and America. Fundamental reviews of mineral deposits in the USSR, USA, Canada, South America, Australia and Japan have proved to be very useful in compiling the book, along with valuable albeit fragmentary descriptions of some deposits in other countries of Europe, Asia and Africa.

Characterization of magmatic formations associated with endogenous mineral deposits is based on the classification proposed by Yu. Kuznetsov. The clarke values were verified in handbooks on geochemistry. Statistics of world production and reserves of ores and metals were taken from reviews on economic geology.

This book is supposed to fill the need of English-speaking specialists interested in current handbooks on applied geology.

The authors would be grateful if this English edition proves useful to readers.

Academician V. I. Smirnov

CONTENTS

FERROUS METALS

Ferrous metals include iron and alloying ingredients such as manganese, chromium, titanium and vanadium, added to iron during the melting process to obtain different alloys.

1 IRON ORE DEPOSITS

Archaeologic pre-historic evidence dates the first application of iron-made articles back to 4000 B. C. At that time iron meteorites found by chance were used to fabricate decorations, working and hunting utensils. An iron girdle at that time had much higher value as compared to a gold one, and only Egyptian Pharaohs could afford a chariot axle made of iron. An iron extraction by smelting ore had started in the first millennium A. D. and the Bronze Age was succeeded by the Iron Age. Metallurgy was in gradual progress. Small furnaces had been originally used for smelting brown iron ore with charcoal. The progress of the ironmaking technique brought about blast furnaces to supercede the smelters, and cast iron production started with the use of various iron ores and coaking coals.

Further development made it possible to convert cast iron into steel. The 19th century was marked by producing steels of high quality. High-carbon stainless, acid- and alkali-resistant steels were being produced by using special alloying additions such as manganese, chromium, titanium, vanadium, nickel, cobalt, boron, tungsten, molybdenum, niobium and tantalum.

Ferrous metals consumption rose rapidly and in the middle of the 20th century it was 5000 times that of the 16th century. At present the total weight of iron and steel incorporated in machines, equipment, construction works as well as transportation and household utensils is around 6 billion tons. World annual iron ore production amounts nowadays to one billion tons and is expected to double at the end of this century. It is more than total world production of all the other ores taken together.

World measured and proved reserves of iron ores are 185 billion tons, the total reserves estimated to be 350 billion tons. About 1/3 of world known and potential reserves are located in the USSR. There are more than 50 countries where iron ores are mined. The leading ore producing countries are: USSR (245 mln tons per annum), Brazil and Australia (about 100 mln tons, each), USA, Canada, France and India (30-70 mln tons). The average price of commercial iron ore (64% Fe) is about 20 US dollars per ton. Iron ore deposits with prospected reserves of a few billion tons are considered as unique, deposits containing a few hundred million tons as large and those of only a few dozen million tons as small. World-wide there are dozens of unique deposits, hundreds of large and thousands of small ones.

Cast iron is produced from iron ore with iron content above 30-50% with a limited amount of harmful impurities: sulphur – up to 0.3%, phosphorus – up to 0.2%, zinc, lead, arsenic and copper – below 0.1% each. The base-to-acid ratio $\left(\dfrac{CaO + MgO}{SiO_2 + Al_2O_3} \right)$ of the

blast furnace burden should be close to or greater than unity, and the silicon ratio $\left(\dfrac{SiO_2}{Al_2O_3}\right)$ should be higher than 1.8-3. Therefore magnesium and calcium carbonates are desirable whereas an abundance of silica is detrimental.

For concentrating ores the lowest (standard) iron content is specified from .14 to 25%, depending on the size of deposit, mode of occurrence, or quality and complexity of ores (that is the presence of associated useful elements and minerals). If an ore or a concentrate sulphur content is in excess of the specified, they undergo agglomeration or sintering which contribute to sulphur elimination. If an excess of phosphorus is present in ore, it is tied up into the slag which can be used for production of the phosphate rich mineral fertilizers.

Rich ores with iron from 57%, silica up to 8-10% and sulphur and phosphorus up to 0.15% each are not generally used as a blast-furnace burden but directly converted into steel in the open-hearth furnaces, oxygen steel-making or Bessemer converters. Rich ores with the highest iron content ($>68\%$ Fe) and pure as to silica ($<2\%$), sulphur and phosphorus ($<0.01\%$ each) as well as other impurities ($<3.3\%$) are used for production of metallized pellets to be converted into steel in the electric furnaces.

GEOCHEMISTRY AND MINERALOGY

Four iron isotopes are known (^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe) ^{56}Fe being the most abundant. After aluminium iron is the most abundant metallic element in the earth's crust. The average iron content in the crust (clarke) is 4.65 w.%. Increased concentrations of iron (up to two clarkes) can be observed in ultrabasic, basic and intermediate, as well as metamorphic rocks.

Clarke of iron concentration defined as a ratio of the average metal content in commercial ore to its clarke is low (about 10).

In compounds iron exhibits two stable valencies; Fe^{2+} is mainly related with endogenous processes, while Fe^{3+} with exogenous ones.
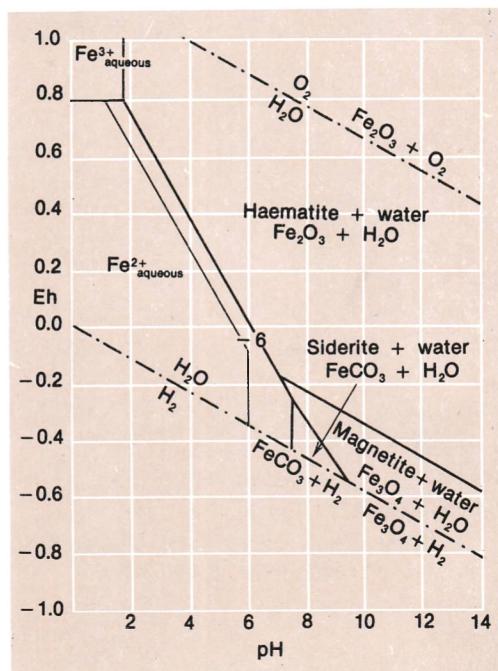
Fig. 1. Stability fields for oxides and carbonates in aqueous solution depending on acidity-alkaline (pH) and redox (Eh) conditions at 25°C and general pressure 1 kgf/cm². (After R. M. Garrels). Isoline lg (dissolved iron)= −4 is shown in a weak solid line. Isoline lg (dissolved iron)= −6 serves as the boundary between solid phase and ions

Endogenous magmatic concentrations of iron can be found in basic and intermediate rocks as well as in genetically interrelated postmagmatic products. Exogenous concentrations of iron are typical of the sedimentary rocks and weathering crusts of the ultrabasic rocks. Emergence of iron compounds with that or other valency and their interrelations are determined by pH and Eh conditions of the environment (Fig. 1).

There are over 300 iron containing minerals. Commercial minerals are: magnetite Fe_2O_3 (72.4%), martite (hematite pseudomorph developed after magnetite) and hematite Fe_2O_3 (70%), brown ironstones such as natural iron hydroxides – goethite (FeO·OH) and hydrogoethite (FeO·OH × × nH$_2$O) in mixture with silica hydroxides and argillaceous ingredients (48-63%), side-

te $FeCO_3$ (48.3%) and sideroplesite (Mg, Fe) CO_3 (45.1%), and iron silicates – chamosite and thuringite (27-38%) *.

METALLOGENY

The main concentration of iron during the geosynclinal cycle occurs predominantly at an early stage when magmatic and skarn iron ore deposits are formed in relation to basaltic magmatism. Sedimentary ores are accumulated in littoral parts of geosynclinal basins at the same stage. The intermediate and late stages of geosynclinal development are of low productivity for iron concentrations. Sedimentary and weathering iron ore deposits are formed during the platform stage of the tectonic cycle.

Iron ore basins with the well developed facies of originally chemogenic, terrigenous-chemogenic and volcanogenic ferro-siliceous sediments, that later metamorphozed to ferruginous quartzites are formed in the Archean-Early-Proterozoic metallogenic epoch. Unique deposits of ferruginous quartzites and iron-rich (martite-hematite) ores developed after them are known in Labrador (Canada), Lake Superior (USA, Canada), Minas Gerais (Brazil), Krivoi Rog and Kursk Magnetic anomaly (USSR), Bihar and Orissa states in India, West Africa, West Australia and East Antarctica. The total iron resources of ferruginous quartzites reach hundreds of billions tons, far exceeding resources of all the other iron ore deposits. Late Proterozoic is characterized by accumulation of hematite oölitic ores in the coastal terrigenous-carbonate geosynclinal marine sediments Clinton in the USA, Angara-Pit in the USSR, Bafing-Bakoy in Mali, deposits in South Africa and North Australia).

The Paleozoic epoch is associated with considerable ferrous mineralization related to Caledonian and Hercynian tectogenesis. It is in this epoch that large magmatic titanomagnetite deposits in the USSR (the Urals) and South Africa, scarn-magnetite deposits in the Urals, North Kazakhstan and West Siberia (USSR), in California,

Utah and New Mexico (USA) and others were formed.

In Mesozoic and Quarternary large sedimentary marine and continental fluvial or lacustrine ferruginous deposits were formed on juvenile epi-Hercynian platforms and plates (West Siberia, Ayatsk and Kerch ore fields in the USSR and Lorraine field in France).

TYPES OF COMMERCIAL DEPOSITS

Commercial iron ore deposits are diverse in origin, they can be found among endogenous, exogenous and metamorphogenous series of mineral deposits and include the following groups: (1) magmatic; (2) carbonatitic; (3) scarn; (4) volcanogenic hydrothermal; (5) volcanogenic sedimentary; (6) weathering crust; (7) sedimentary; and (8) metamorphogenous.

MAGMATIC DEPOSITS

Typical titanomagnetite and ilmenite-titanomagnetite deposits in the USSR are known in Karelia (Pudozhgora), the Urals (Kachkanar, Gusevogora, Pervouralsk, Kopansk, etc.), Mountainous Altai (Kharlovsk), Eastern Sayan (Lysansk, Kruchinino and Malyi Tagul); they can also be found in Tegavus (USA), Taelness (Norway) and Taberg (Sweden).

Ore bodies occur as zones of dense impregnation with schlieren and vein-lens-like segregations of titanomagnetite in intrusions of gabbro-pyroxenite-dunite, gabbro, gabbro-diabase and gabbro-anorthosite formations.

Titanomagnetite with the texture of disintegration of the solid solution, composed of magnetite with the fine-plated intergrowth of ilmenite, is the main ore mineral in this group of deposits. Magnetite, ilmenite and spinel grains are present in subordinate quantities. Rock-forming minerals of country rocks such as olivine, pyroxene, amphibole, plagioclase, serpentine, etc. occur as accompanying minerals.

Commercial iron, vanadium and in some cases also titanium contents are characteristic of this type of deposits as well as

---

* The content of principal metal is here and later used in brackets.
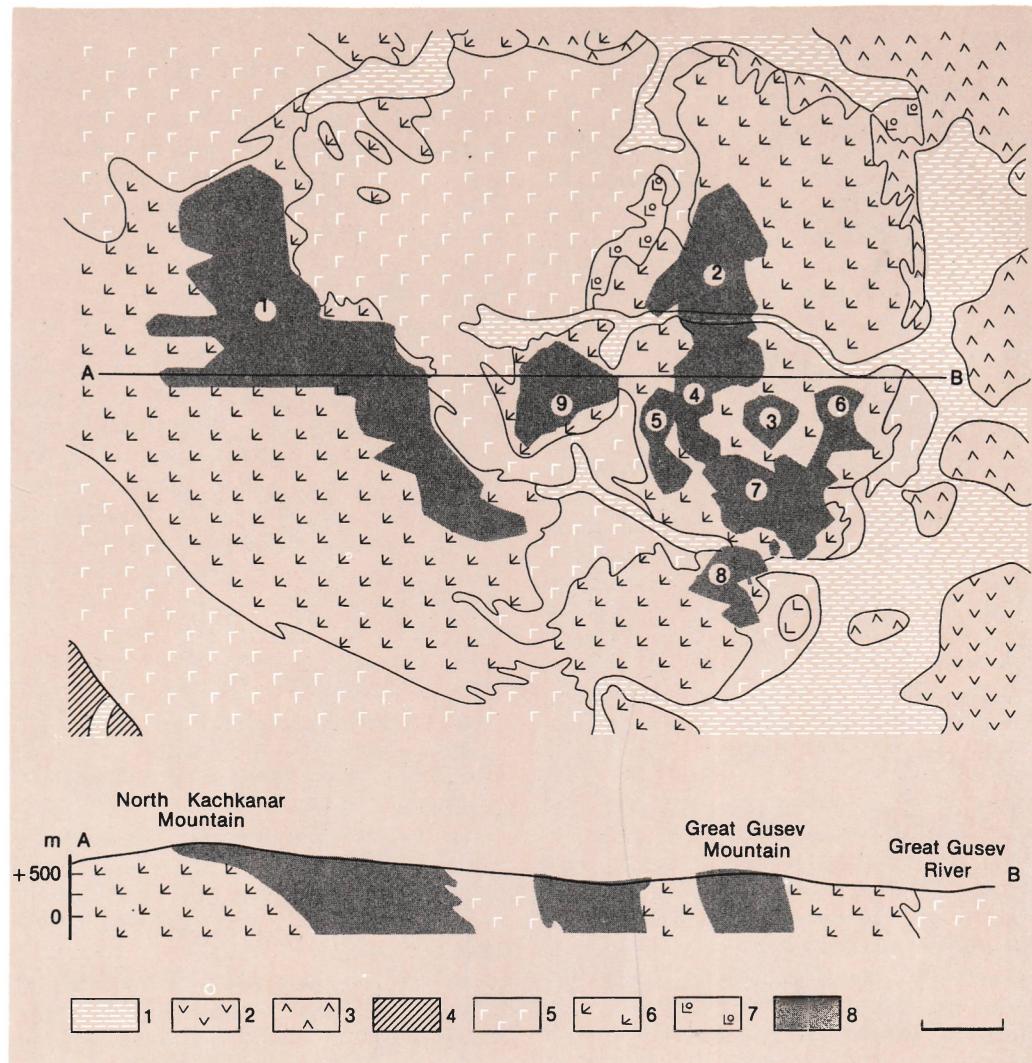
Fig. 2. Geological structure of the Gusevogora and Kachkanar titanomagnetite deposits. (After Z. Rupasova):

1 – alluvium;
2 – porhyrites;
3 – amphibolites;
4 – albite-chlorite and other Ordovician schists;
5 – gabbro;
6 – pyroxenites;

7 – hornblendite;
8 – ore bodies.
Numbers in circles;
1 – Kachkanar deposit;
2 – Gusevogora deposit;
3-9 – sectors of Gusevogora deposits

low sulphur and phosphorus contents (hundredths of a per cent), and dispersed platinum.

KACHKANAR. This deposit is located in Isovskii district of Sverdlovsk region. The area of Kachkanar ore-bearing gabbro-pyroxenite pluton is about 110 km². It has an isometric configuration and is considered to be of the laccolith group (Fig. 2). Plagioclase porphyrites and effusive silurian diabase are the enclosing rocks of the pluton at its eastern boundaries, Ordovician micaceous and siliceous schists are the country rocks at the western boun-

...ry. In the northern and southern peripheral parts of the pluton, gabbro is substituted with amphibolite. Nearly half of the area of intrusive rock is composed of pyroxenite which forms two massifs: Gusevogora at the east and Kachkanar at the west.

Kachkanar pyroxenite massif that also includes olivinite and peridotite is extended 15 km north-eastward and its average width is 3.2 km.

Gusevogora pyroxenite massif which is partially composed of peridotite, hornblende and gabbro is extended in meridional direction, being 8.5 km long and 1-4 km wide. There are nine ore bodies in Gusevogora deposit, only the Main and West ore bodies (with commercial grade mineralization area of 2 km²) being mined at present. Low-grade ores (non-commercial) and barren patches (usually isometric in configuration, with the area of 1 000 to 2 200 m²) have been located within the contour of commercial mineralization. The mineralization depth is 600 m and more.

Both ore-bearing and barren pyroxenites are intersected with multiple hornblende and quartz plagioclasite dikes up to two metres thick, having variable strikes and dip angles from 20 to 90°. Ore bodies are composed of titanomagnetite impregnations, in some cases of schlieren segregations and veinlets of massive ores in host rocks, mainly represented by pyroxenite, gabbro and hornblendite, and, only occasionally, by peridotite and olivinite. Ores in this deposit are classified into five natural types: coarse- (exceeding 3 mm), average- (1-3 mm), fine- (0.2-1 mm), ultrafine- (0.05-0.2 mm) and dispersely-impregnated (finer than 0.05 mm).

Titanomagnetite is the main ore mineral, having the solid solution disintegration structure and containing 2-18% ilmenite as well as isomorphic vanadium admixture. Accompanying ore minerals are pyrite and pyrrhotite; in some rare cases chalcopyrite, pentlandite and bornite as well as native platinum and platinoids can be found. The following gangue minerals are present in the deposit: pyroxene, amphibole, olivine, serpentine, plagioclase; in some cases, epidote, apatite, zoisite and chrome spinel together with pyroxene and amphibole

alteration products, that is chlorite and biotite.

Valuable components content in the ores is low: Fe 15-18 w.% (commercial above 14 w.%); phosphorus and sulphur are practically absent. In a course of metallurgical processing of the iron-vanadium concentrate vanadium is recorded in addition to cast iron by means of extraction from converter slags.

The reserves of Gusevogora and Kachkanar deposits are estimated as 3.5 and 2.6 billion tons respectively, with the average iron content in the ores of 16.6%.

CARBONATITE DEPOSITS

Perovskite-titanomagnetite and apatite-magnetite deposits located in alkaline-ultrabasic intrusive massifs of the central type are known from the Baltic Shield (Afrikanda, Kovdor) and Siberian platform (Gulinsk massif) in the USSR, as well as from the African platform (Sukulu in Uganda; Dorova in Zimbabwe, and Lulecop in South Africa).

Iron ores, with ore minerals represented by titanomagnetite and cerium perovskite-knopite, are chiefly located in the central part of an intrusion. In intrusions characterized by considerable development of carbonatites apatite-forsterite, phlogopite-forsterite, apatite-calcite and calcite accumulations are developed after ultrabasic rocks. Bodies of iron ore in such massifs are mainly composed of apatite-forsterite rocks with dense magnetite impregnations in the form of veins and streaks, and irregular impregnations of pyrochlore and baddeleyite.

Magmatic genesis with the subsequent metasomatic development is most probable for perovskite-titanomagnetite deposits in intrusive rocks with predominance of ultrabasites and only slight development of carbonatites. Apatite-magnetite deposits in intrusions with a considerable development of carbonates are considered by some authors as metasomatic accumulations.

KOVDOR. The deposit is situated in Kirovsk district of Murmansk region and is restricted to Kirovsk massif of ultrabasic-alkaline rocks and carbonatites with
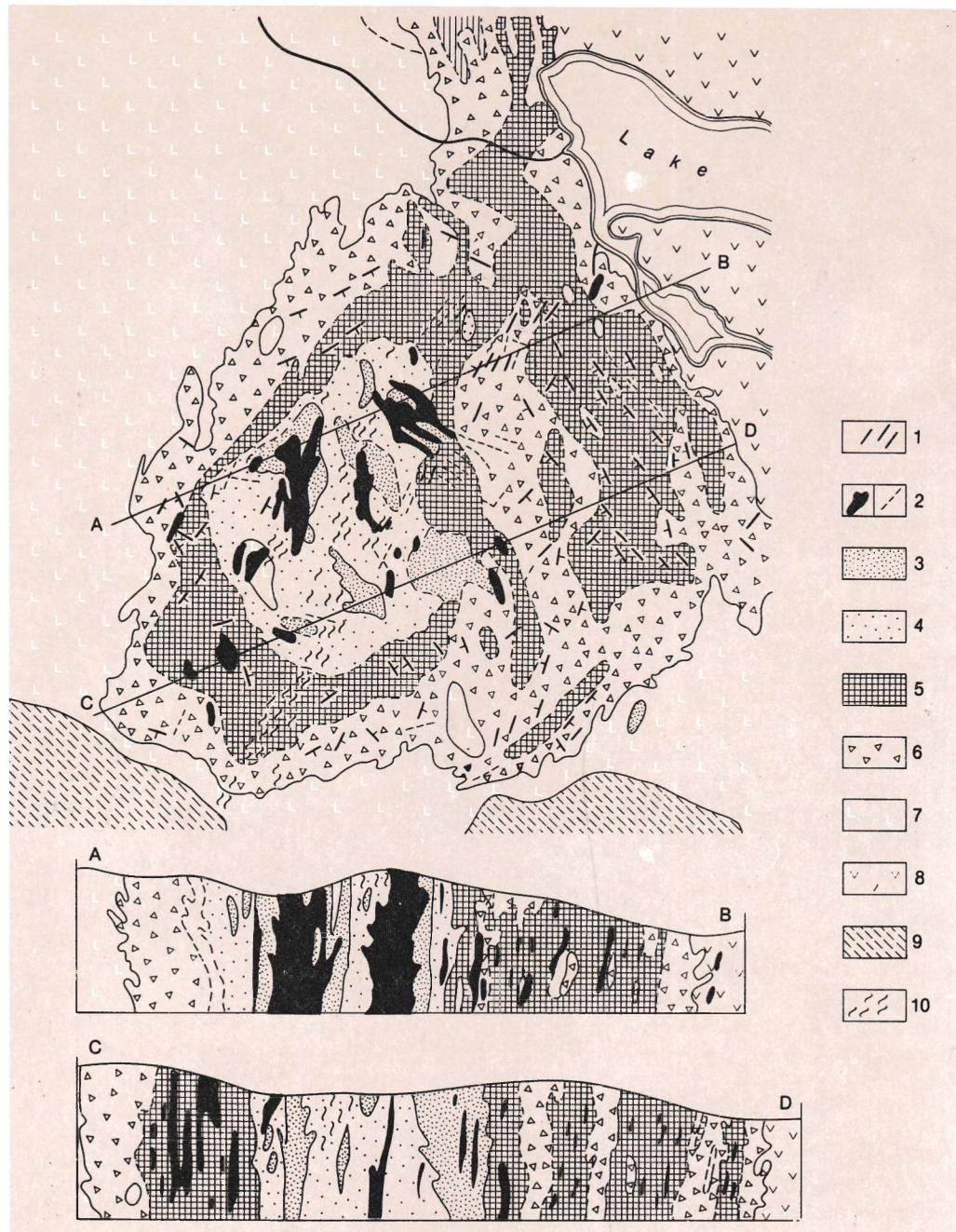
Fig. 3. Geological structure of the Kovdor magnetite deposit. (After V. Namoyushko, A. Mikheevich and O. Rimskaya-Korsakova):

1 — dolomite carbonatites;
2 — calcite carbonatites
(a — irregular bodies; b — vein bodies);
3-5 — ores:
3 — apatite-forsterite-magnetite;
4 — forsterite-magnetite;

5 — phlogopite-apatite-forsterite-magnetite;
6 — apatite-forsterite rocks;
7 — ijolite-urtite, ijolite and melteigite;
8 — pyroxenite;
9 — fenite;
10 — segregations of staffelite

an area of 40 km². The massif is a multi-phase intrusion of the central type and consists of consecutively intruded olivinites, ijolites, melteigites, and nepheline syenites together with a complex of silicate metasomatites and carbonatites.

Magnetite ore and magnetite-bearing rocks make up the ore body which is extended in submeridional direction and is 1.3 km long and 100-800 m wide, in the south-western part the massif is enclosed with ijolites and pyroxenites (Fig. 3). This ore body has been explored down to 600-700 m.

The ore body is surrounded by a solid fringe of phlogopite-apatite-forsterite rocks 20 to 120 m wide, separating ore body from enclosing ijolites and pyroxenites. These rocks in the form of pockets and lenses also occur within the ore body, often being turned into carbonatites.

The deposit contains ores with low calcite content such as apatite-forsterite-magnetite, forsterite-magnetite and phlogopite-apatite-forsterite-magnetite. As to their structure the ores are classified into banded, impregnated, spotty and massive. The texture of ores is xenomorphic-granular. The grain dimensions vary from 0.5-5 mm up to a few centimetres. Magnetite typically has inclusions of olivine, apatite, calcite and spinel. Other ore minerals such as ilmenite, pyrrhotite, chalcopyrite, pyrite and marcasite only occur in small quantities. Sulfides are irregularly disseminated. Increased contents of magnesium oxide (4.7-7.9%) and alumina (2-4.4%) are characteristic of magnetite, therefore magnetite disintegration results in spinel formation. In all the types of iron ores as well as carbonatites irregular fine impregnations of pyrochlore and baddeleyite are present.

The ores composition (w.%) is as follows: Fe 20-55 (the average 29); MgO 15-17; CaO 11-12; P 2.9; S 1.2; MnO and TiO_2 – tenths fractions of a per cent.

Kovdor deposit prospected reserves of magnetite ores are estimated as 700 mln tons. In addition to magnetite concentrate both apatite and baddeleyite concentrates are recovered from the ores of this deposit.

SKARN DEPOSITS

Skarn-magnetite deposits are widespread in the USSR in the Urals (Vysokaya Gora, Gora Blagodat, North Peschansk, etc.), in Kustanai region of Kazakhstan (Sarbai, Sokolovsk, Kachar, etc.), in West Siberia (Tashtagol, Abakan, Teya, etc.), in the Caucasus (Dashkesan), they can also be found in the USA (Iron Springs, Adirondack, etc.), the Central Europe (Erzgebirge), Italy, Bulgaria, Rumania, Japan, China and other countries. Skarn-magnetite deposits are related to plagiogranites which are regarded as products of basaltic magma at the early stage of geosynclinal development.

According to geologic environment G. Sokolov classified skarn deposits into lime-skarn, magnesian-skarn and magnesian-lime-skarn, scapolite-albite and scapolite-albite-skarn, magnetite and hematite hydrosilicate which could be considered as formations of skarn iron ore deposits.

Mineral association of deposits of lime-skarn formation is represented by minerals of pyroxene-salite and garnets of andradite-grossularite type as well as by epidote, zoisite, actinolite, vesuvian and chlorite; ferruginous minerals are typified by magnetite, muschketowite, martite and hematite; sulfide minerals are known in a form of cobalt-containing pyrite, perrhotite, chalcopyrite, sphalerite and galena, etc. Late gangue minerals are represented by calcite and quartz veinlets. Deposits of this formation are known in the Urals, Caucasus, Altai, in Kazakhstan and Central Asia.

Magnetite deposits of magnesian-skarn formation are mainly located in ancient shields and Precambrian folded area. For mineral associations of magnetite magnesian-skarn deposits it is typical to observe development of magnesian silicates such as forsterite and alumina diopside-fassaite, spinel, phlogopite and serpentine. Deposits of this formation are situated in Kuznetsk Ala-Tau (Teya) and Gornaya Shoriya (Sheregesh). Some geologists (L. Shabynin et al) consider iron ore deposits of Yakutia (Tayozhnyi, etc.) as magnesian-skarn, but other geologists distinguish them as contact-

metamorphosed sedimentary formations (V. Pervago et al).

Intensive chlorine-sodium metasomatism, which manifests itself in formation of scapolite-albite metasomatites replacing alumosilicate rocks within the ore field, is the main distinguishing feature of scapolite-albite and scapolite-albite-skarn magnetite deposits. Mineral associations of deposits of this formation differ from above deposits in development of scapolite, albite, and less typical anhydrite together with much more common zeolite. The unique skarn-magnetite ore deposits in Kustanai Region (Sarbai, Sokolovsk and Kachar deposits) pertain to deposits of this formation.

Magnetite and hematite hydrosilicate metasomatic deposits are often situated in ore fields along with skarn deposits, but far off intrusive contacts. According to mineral composition the temperatures of formation of near-ore metasomatites and ores of hydrosilicate deposits were much lower as compared to skarn deposits. Near-ore metasomatites are composed of epidote, actinolite, in some cases albite, garnet, pyroxene, chlorite, zeolite, calcite (and other carbonates), and quartz. Magnetite (sometimes hematite in the form of iron glance) is the main ferruginous mineral. Abakan deposit in Khakassia is a typical example of this group.

SARBAI. This deposit was discovered in 1948 as a result of sharp magnetic disturbance observed on airplanes in this region. It is situated in Trans-Urals Steppe at 45 km south-west from Kustanai. The deposit is composed of three ore bodies: Eastern, South-Eastern and Western (Fig. 4).

Ore bodies are located among metasomatites formed after volcanogenic-sedimentary deposits of Valerian subzone represented by stratified Low-Carboniferous andesite porphyries and their tuffs, tuffaceous breccias, tuffites, limestones, sandstones, tuffaceous sandstones, as well as Middle- and Upper-Carboniferous hematized tuffs and tuffaceous lava of basalt composition, tuffites and argillites. Above rocks form Sokolovsk-Sarbai anticline with submer-idional strike. Ore bodies of Sarbai deposit

are situated in the western limb, but bodies of Sokolovsk deposit are located in the Eastern limb of the anticline.

Premineral, intramineral and postmineral dislocations are widespread in the deposit area. The diorite-porphyrite dikes are intruded along the premineral, submeridional faults with the dip angles 65-70° to the west. The intramineral disjunctive dislocations are marked by the vein-like skarn-magnetite segregations crossing the bedding. Postmineral faults resulted in block displacements of the ore bodies, and granulation of ores and enclosing metasomatites. Some of the postmineral faults are intruded by the dikes of quartz diorite-porphyrites and granite-porphyrites.

Transformations of parent rocks within the deposit are represented by premineral hornfelsation, formation of biotite-potassium feldspar and albite metasomatites, and development of co-mineral metasomatites such as pyroxene-scapolite, pyroxene, garnet, scapolite-pyroxene-garnet and epidote-actinolite, as well as postmineral metasomatites such as chlorite-prehnite-calcite-quartz and zeolite.

The ore bodies of the Sarbai deposit are constituted of sheet-like beds conformable with the host rock stratification. The ore bodies are either tapering as a result of gradual transition into barren metasomatites or cut off by large amplitude postmineral faults. The length of the ore bodies is from 1 000 to 1 700 m with the thickness up to 170-185 m, their dip being traced down to 1 800 m.

The ores of the deposit are composed by halves of massive varieties ($>50\%$ Fe), the other half being represented by impregnated ores (20-50% Fe). Alternation of massive and impregnated ores with barren metasomatites is observed here. All ores have magnetite composition. Sulfide ores such as pyrite, pyrrhotite-pyrite with low content of magnetite, chalcopyrite and sphalerite are found here in subordinate amounts.

Massive and impregnated magnetite ores have banded and coarse-banded structures inherited from structures of primary calcareous tuffites and limestones. Besides prevailing magnetite, such minerals as pyroxene, scapolite, garnet, wollastonite,
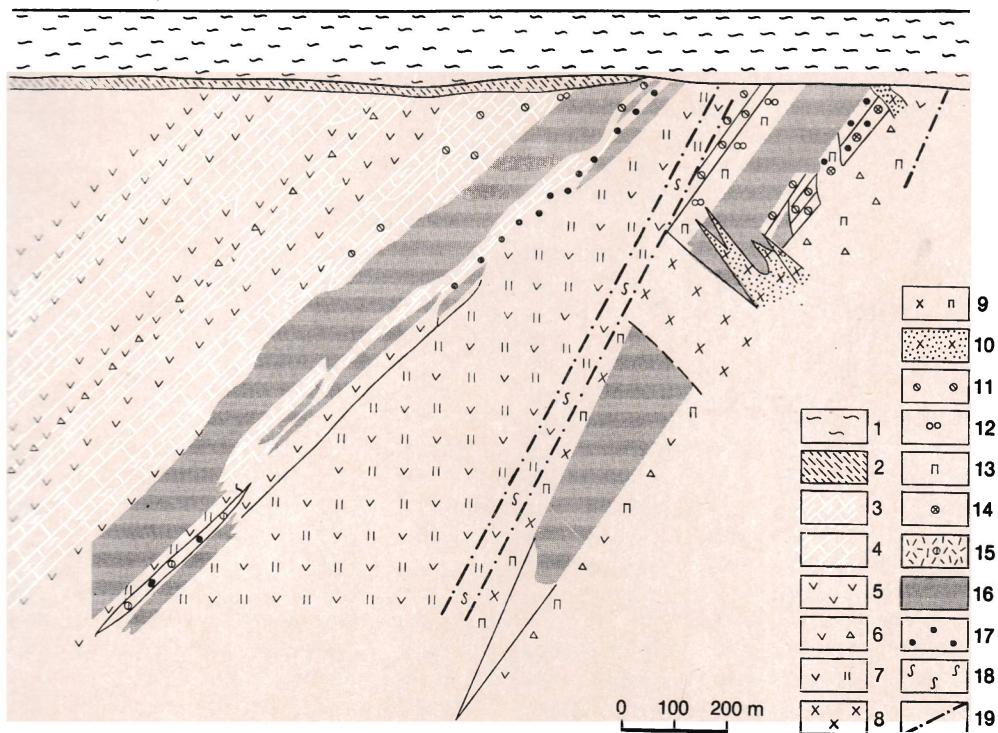
Fig. 4. Geological section of the Sarbai magnetite deposit. (After I. Kochergin):

1 – Meso-Cenozoic sediments;
2 – clays of ancient weathering crust of Paleozoic rocks;
3 – tuffites;
4 – limestones;
5 – tuffs;
6 – tuffs and breccias;
7 – brecciated tuffs;
8 – diorites;
9 – diorite porphyrites;
10 – post-ore diorite porphyrites;
11 – hornfelsed tuffites;
12 – scapolitic metasomatites;
13 – pyroxene skarns;
14 – garnet skarns;
15 – epidote-actinolite rocks;
16 – massive magnetite ores;
17 – disseminated magnetite ores;
18 – rock and ore mylonitization zones;
19 – faults

albite, epidote, actinolite, apatite, pyrite, calcite, quartz, accessory vesuvian and sphene occur in the ore. Accompanying minerals are pyrrhotite, arsenopyrite, sphalerite, galenite and chalcosine. Micaceous hematite and muschketowite are found in minor quantities. Prospected reserves in the deposit run to 700 mln tons with the average iron content 45.6, sulphur 4.05 and phosphorus 0.13%.

The total potential reserves apparently amount to 1.5 bln tons on account of the deep horizons of the Western and Eastern ore beds.

VOLGANOGENIC HADROTHERMAL DEPOSITS

Hydrothermal magnesium magnetite deposits paragenetically related to the trapps are known on the Siberian platform. Here they form a number of iron-bearing regions: Angara-Ilim, Angara-Kata, Middle-Angara, Kansk-Taseyevo, Tunguska, Bakhta and Ilimpeya. Korshunov, Rudnaya Gora, Neryundinsk and Tagarsk deposits are the largest prospected ones in this group.

The deposits are situated in Paleozoic sediments of the platform cover. They occur within the part of a region composed of

intrusive trapps of the Siberian platform, where the lower strata of the platform sediments contain halogenic sediments, the presence of these being indicated by formation of iron chlorides and their subsequent migration into overlying rocks.

The distribution of the magnesium-magnetite deposits within the platform is closely related to the fault zones and areas of intensive development of trapp magmatism. Such zones form two belts: (1) with the north-west strike along the western margin of the trapp region (from the middle streamflow of the Angara river on the southeast to the Kureika river on the north); (2) with the north-east strike along the southeastern margin of the Tunguska syneclise.

Solutions were penetrating along tectonic faults and, apparently, volcanic pipes bringing about metasomatic alteration and mineralization. Metasomatic processes resulted in the development of skarn-like and lower-temperature chlorite-serpentinite-carbonate metasomatites.

The ores are represented by impregnation zones in metasomatites, vien-shaped bodies and sheet-like formations of metasomatic substitution after carbonate rocks. Argillite, fine-grained limestones and trapp sills were acting as "screens" during the formation of the sheet-like deposits. Ore-forming magnetite at all times contains isomorphic magnesium admixture and is identified as magnesium magnetite variety. With the increase of the formation depth magnesium content in magnetite is decreasing due to the drop of oxygen potential of the ore-forming solutions since entree of magnesium into magnetite molecule occurs as a result of partial oxidation of ferrous ions into ferric ones.

KORSHUNOV DEPOSIT. The deposit is situated in Zheleznogorsk district of Irkutsk region on the main railway Taishet-Lena.

The deposit is localized in sediments of the platform cover composed of argillites, limestones, marls, aleurolites, sandstones and Upper Cambrian and Ordovician clays. Intersections between the sedimentary rocks and the steeply dipping tectonic faults are filled with brecciated tuffs and debris of enclosing rocks subjected to considerable metasomatic alteration. Igneous rocks of the region are represented by trapps which form steeply dipping dikes of the north-east (in some cases latitudinal) direction, and by sheet-like bodies with the thickness of 30 m and more, both being composed of gabbro-dolerites, dolerites and doleritic porphyrites (Fig. 5).

In metasomatically transformed pyroclastic rocks one observes stock-, lens-, sheet- and pillar-like metasomatic ore bodies along with the steeply dipping veins of massive magnetite. The main ore body is elongated from the south-west to the north-east on 2.5 km, being 400-600 m wide. The ore bodies are tapering with depth and have been traced down to 1 100 m.

The brecciform and disseminated ores associated with surrounding metasomatites by gradual transitions are widespread. Massive and banded ores are rarely encountered. The main ore mineral is magnomagnetite which contains up to 6% of magnesium oxide. Hematite is the subordinate ore mineral. The metasomatites surrounding the ore and the ore itself also contain diopside, garnet, epidote, apatite, chlorite, calcite, actinolite, flogopite, hornblende, talc, zeolite, montmorillonite and aragonite.

The prospected reserves are estimated to exceed 400 mln tons with average contents of iron being 34.4%, sulphur 0.02% and phosphorus 0.2%.

Fig. 5. Geological structure of the Korshunov magnetite deposit. (After M. Ivashchenko and V. Korabelnikova):

1 – Quaternary sediments;
2-5 – magnetite ores:
  2 – vein;
  3 – massive;
  4 – banded;
  5 – disseminated and brecciated;
6 – near-ore metasomatites;
7 – traps;
8-14 – volcanic and sedimentary rocks:
  8 – tuffaceous;
  9 – Middle Bratsk member;

10 – Low Bratsk member;
11 – Upper Mamyr member;
12 – Low Mamyr member;
13 – Ust-kut member;
14 – Upper Lena member;
15-17 – rock contacts:
  15 – eruptive;
  16 – diffusion;
  17 – stratigraphic;
18 – faults

1	8		
2	9		
3	10		
4	11		
5	12	15
6	13	16
7	14	17	18
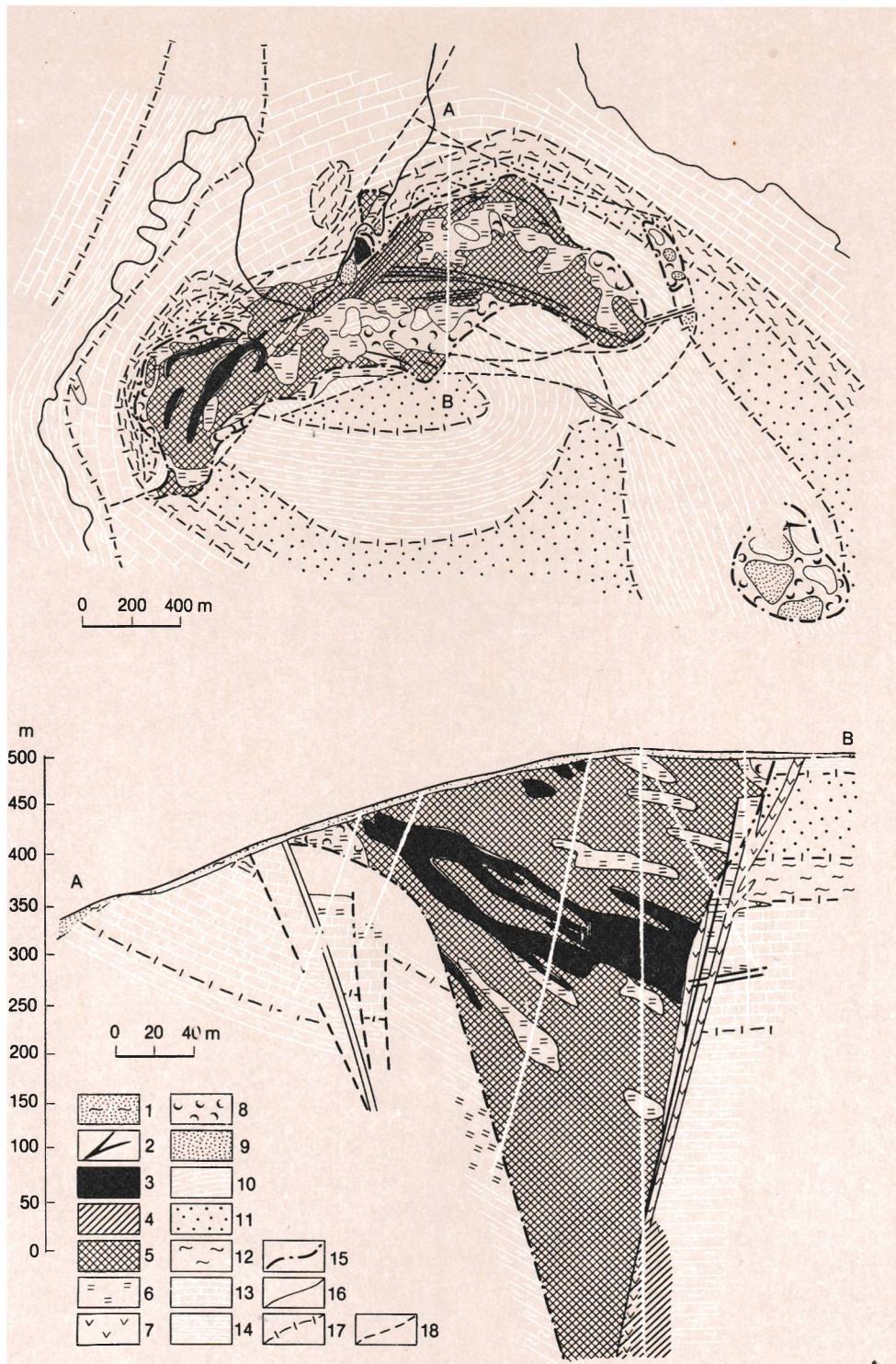
VOLCANOGENIC-SEDIMENTARY DEPOSITS

The deposits of this group comprise those in Western Karazhal in Central Kazakhstan, Kholzun in Mountainous Altai, and the Tersin group of deposits in Kuznetsk Ala Tau as well. In other countries this type of deposit is represented by the Lahn and Dill deposits in FRG, Gara Dzhebilet and Mesheri Abdelazis in Algeria. The deposits are located in synclinal zones of eugeosynclinal formations. Some of them, as for example, the Kholzun deposit, demonstrate the most intimate relation to volcanogenic facies of the volcanogenic-sedimentary formations, which is manifested by deposition of the ore beds among tuffs and tuffites with interlayers and lenses of volcanic rocks in the ore beds themselves. This close relationship is also expressed in the presence of pyroclastic particles in the ore composition. Other such deposits, as for example, the Atasu (Western Karazhal and others) are characterized by the interbedded limestones, siliceous-carbonate jaspery and argillite rocks that enclose ore beds and lenses. The ore-bearing strata are underlain by typically volcanogenic-sedimentary formation.

Ore beds and lenses together with enclosing rocks are deformed by folds and faults which determine their conformable setting in the folded structures of the ore fields. In the Kholzun deposit, such a structure is intruded by granitoids which brought about a contact-hydrothermal metamorphism at certain parts of the field with formation of skarn-magnetite ores.

The ores are composed of hematite, and to a lesser extent, of magnetite and siderite. They also contain sulfides, such as pyrite, arsenopyrite, chalcopyrite, sphalerite and galenite. Among gangue minerals one finds chlorite, sericite, quartz, chalcedony, opal, dolomite, ankerite, apatite, and in weakly developed zones of oxidation there are also martite, goethite and hydrogoethite.

The commercial importance of the deposits belonging to this group is not significant. If, however, very large scapolite-albite and scapolite-albite-skarn magnetite deposits found in Kustanai region are included in this group, as some of the geologists consider, the importance of the group sharply rises.

THE WESTERN KARAZHAL DEPOSIT. This deposit is located 110 km south-west of the Zhana-Arka station in the Karaganda region of the Kazakh SSR. The deposit belongs to the Atasu iron ore field.

The geological structure of the deposit is composed of a thick suite (up to 1.5 km) of volcanic and tuffogenic rocks of Lower and Middle Devonian, as well as by an Upper Devonian-Lower Carboniferous suite of sedimentary rocks of the same thickness of the Dzhailmin trough.

Volcanogenic-sedimentary rocks are composed of lavas of trachyte and liparite compositions accompanied by pyroclastic sediments, sandstones and schists. The suite of sedimentary rocks is represented in the lower part by coaly-siliceous and coaly-clayey-siliceous limestones containing interlayers and lenses of siliceous jaspery rocks, volcanics of spilite type, their tuffs and lava breccias and also beds and lenses of magnetite, hematite and manganese ores.

The middle and upper parts of the section consists of siliceous-clayey-carbonate and jaspery rocks. The rocks of the suite go down up to 600-m depth dipping at 45-50°, with further sharp submersion. The igneous rocks are represented by dikes of diorites and dioritic porphyries which intersect both volcanic and sedimentary deposits.

The ore body itself has sheet-like shape and lies in conformity with host rocks. Its strikewise length is 6.5 km, and the length along dipping is 800 m. The thickness of the body is 20-40 m, it decreases at the western flank to a complete wedging out (Fig. 6). The ore bed occurs between coaly-siliceous limestones having the interlayers of jasper in the footwall, and limestones with the interlayers of jaspery rocks, in the hanging wall. In the lower part of the ore body hematite ores are developed whereas in the middle part magnetite is mainly located. The upper part of the ore body is composed of low-grade hematite manganous ores. At the base of the ore bed there is a thin manganese-ore seam. Similar seams and lenses of manganese ore are also found
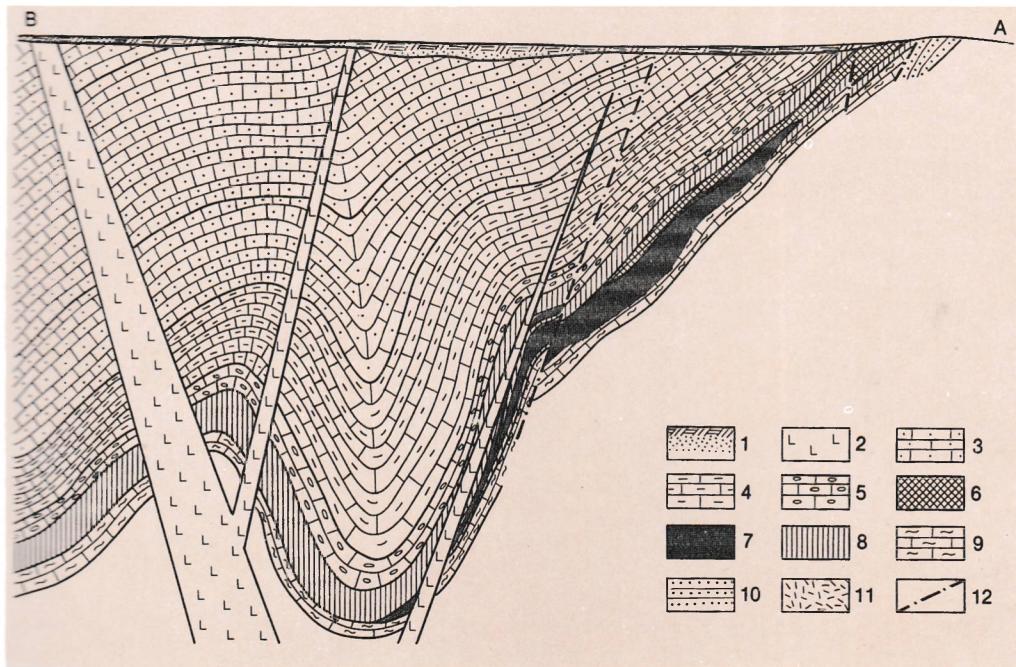
Fig. 6. Geological cross section of the Zapadny (West) Karazhal hematite-magnetite deposit. After G. Momdzhi, V. Kavun and S. Chaikin):

1 – Quaternary loams;
2 – dioritic porphyries;
3–5 – limestones:
3 – siliceous;
4 – carbonaceous;
5 – with interbeds of hornblende;
6–8 – ores:

6 – magnetite;
7 – hematite;
8 – ferromanganese;
9 – siliceous-carbonate rocks;
10 – sandstones;
11 – quartz porphyries;
12 – faults

inside hematite beds. In the upper parts of the deposit there is a zone of baritized iron ores.

The deposit contains three commercial types of ores, i.e. magnetite, magnetite-hematite, and hematite. The first two types are distinguished by high contents of germanium. The main ore forming minerals are hematite and magnetite. The subordinate minerals are siderite, barite, and pyrite. There are smaller quantities of arsenopyrite, chalcopyrite, sphalerite and galenite. The oxidation zone of the deposit which is traced down over a few tens of metres, contains martite and iron hydroxide minerals. The structures of the ores are banded and massive. Their textures are granular, and porphyroblastic.

The prospected reserves of the ores exceed 300 mln tons with average contents (w. %) of Fe 55.6, SiO_2 12.4, S 0.6, and P 0.03.

DEPOSITS OF WEATHERING

The deposits of weathering are represented by the goethite-hydrogoethite (brown iron ore), martite-hydrogoethite zones of oxidation in the deposits of siderite and skarn-magnetite ores and also by weathering crusts in ultrabasic rocks. The formation of oxidation zones was related to the ancient and modern weathering epochs.

Siderite ores in an oxidation zone are altered into a mixture of iron hydroxide minerals (such as goethite, hydrogoethite, hydrohematite, and turgite), which contain also calcite and subordinate minerals, such as psilomelane and pyrolusite. There are also rare minerals, which include aragonite, gypsum, marcasite, malachite, azurite, cuprite, native copper, sometimes scorodite.

At the expense of alterations of skarn-magnetite ores, martite-hydrohematite

ores are formed, which depending on distribution of skarn and post-skarn silicates and sulfides in primary ores contain nontronite, halloysite, allophane, boehmite, calcite, aragonite, cuprite, covellite, malachite, azurite, chrysocolla, psilomelane, and erythrite, and others.

The deposits of goethite-hydrogoethite ores represent the upper ochreous zone in the weathering crust of serpentinized dunite and peridotite massifs, which is substituted downwards by the zones of silicified, leached, nontronitized and carbonitized serpentinites (magnetite is formed here). Sometimes, the above deposits are accompanied with redeposited ores being lake depositions of washout products from weathering crusts. The latter have the shape of beds and oölitic structure.

Iron ores of weathering crusts over ultrabasic rocks are composed mainly of hydrogoethite and the admixtures of chalcedony, opal, nontronite, ferruginous chlorites, magnesite, relict accessory chrome spinelids, and dusty magnetite. They contain the admixtures of chromium, nickel and cobalt and are classified as naturally alloying products.

The naturally alloying ochreous oölitic ores in weathering crusts, in association with sedimentary ores, are represented by the Yelizavetinskii and Serovskii deposits in the Northern Urals, by the Ackermanovka, Novo Kievka, Novo Petropavlovsk and other deposits in the Southern Urals, and by the Malka deposit in the Northern Caucasus. In other countries large iron-ore deposits in weathering crusts are known in equatorial regions of the globe, such as in Cuba, Hawaii, Guinea, Philippines, Guyana and Surinam.

ACKERMANOVKA DEPOSIT. This deposit, which is a part of the Orsk-Khalilov group of deposits of naturally-alloying iron ores, is located 20 km west of the town of Orsk and is confined to the south-western fringe of the Tanalyk-Baymak Mesozoic depression. The base of the depression is composed of Paleozoic and older folded complexes of the Urals which are intruded by massifs of basic and ultrabasic rocks.

The Paleozoic rocks in the area of the deposit are represented by Tournaisian siliceous shales and by Visean karstic limestones. Triassic-Jurassic weathering crusts are developed over the Paleozoic rocks and serpentinites, enclosed in them.

Limestones and siliceous shales with a sharp disconformity underlie Jurassic continental sediments composed of crushed deluvium, sand, clay, pebble and containing two ore horizons, namely, the lower siderite and upper goethite-hydrogoethite (Fig. 7). The ore bodies of the lower horizon are sheet-like, the ores contain wedging-out clay interlayers. The thickness of the ore body in its central part is about 35 m being reduced to the periphery of the body. The series is composed of siderite-clay and siderite-hydrogoethite oölitic-brecciform ores. The siderite in the ore is subjected to various degrees of oxidation. The deposits of the upper ore horizon fill karstic depressions in limestones, which makes the thickness of the ore body abruptly changing from 1 to 50 m, being in average 14 m. The upper horizon partially rests on slightly karstic limestones and clays, having regular sheet-like form. The upper horizon is made of ochreous-clay, lump-debris (containing fragments, concretions and geodes), conglomerate-oölitic and pebble hydrogoethite-hydrohematite ores.

The Ackermanovka ores, beside hydroxides of iron and siderite, contain ferruginous chlorites, nontronite, manganese minerals, carbonates, gypsum, barite, pyrite, quartz, chalcedony, opal, hydromica, clayey minerals and minerals containing alloying admixtures of nickel, cobalt, chromium (such as revdinskite, nickel nontronite, asbolan, erythrite and chrome spinelids).

On the average the siderite ores contain (w. %) Fe 27.1, Ni 0.29, Cz 1.43. Average iron content in the hydrogoethite-hidrohematite ores is 32%. Among the ores there are high-grade ores which contain more than 35% of iron, about 0.4% of nickel, and more than one % of chromium. The prospected reserves of the ores are estimated to be about 300 mln tons.

SEDIMENTARY MARINE DEPOSITS

In marine terrigenous-carbonate sediments siderite sheet-like deposits are known in the
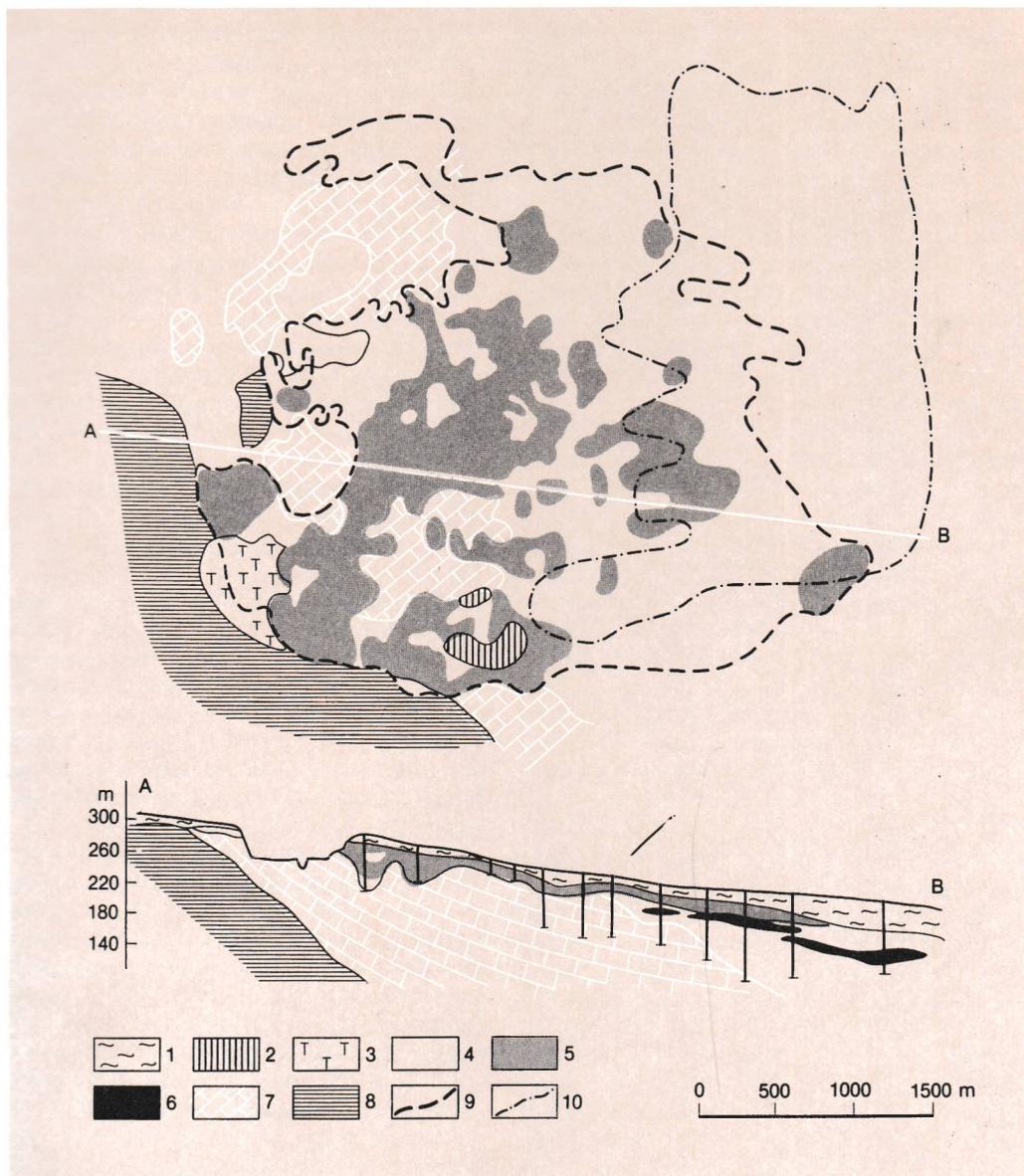
Fig. 7. Geological structure of the Ackermanovka iron ore deposit. (After G. Kiselev):

1 – loams;
2 – redeposited iron ores;
3 – clays, sands and gravels;
4 – sandy clays;
5 – brown iron ores;

6 – siderite ores;
7 – Visean limestones;
8 – charty shales;
9 – boundary of the brown iron ores;
10 – boundary of the siderite ores

western slope of the Southern Urals in the ancient core of the Hercynian anticlinorium. They occur in the oxidation zone and are replaced by brown iron ore in the Proterozoic shale-carbonate sediments. The largest deposits of this type are located within the Bakal region, a number of smaller deposits are also known in the Komarovo-Zigazin and Katav-Ivanov regions.

The Bakal group of deposits consists of over 200 ore bodies occurring as sheet-like, lenticular and nest-like deposits and ore veins. The presence of the latter, as well as remnants of dolomites inside siderite beds, and also the presence of sulfide mineralization, allow sone geologists to consider that these deposits are of hydrothermal origin. However, the majority of investigators believe that the deposits under discussion are sedimentary, and the specifics mentioned above can be explained as a result of secondary superimposed hydrothermal processes.

Geosynclinal marine hematite deposits in terrigenous-carbonate sediments are known in the Angara-Pit ore basin on the right bank of the Angara river. The ore deposits in this area appear to be coastal facies of the Upper Proterozoic geosynclinal sediments. Similar deposits are also known in the USA (Clinton in the Appalachian Mts), in Africa (Bafing-Bakoy basin in Mali) and in North Australia.

Platform marine sediments of siderite-leptochloride-hydrohematite bean-oölite ores in carbonate terrigenous sediments are represented in the Soviet Union by three Meso-Cenozoic ore basins, i. e. the Kerch, Ayat and West-Siberian. Ore-bearing formations belong to the suites of the marginal troughs of the Alpine folded area (Kerch basin), or that of the sedimentary cover of the West-Siberian Epipaleozoic plate (Ayat and West-Siberian basins).

The flat-lying ore beds belong to the coastal-marine facies of Upper Cretaceous, Paleogene and Neogene. The Kerch and Ayat basins have one ore-bed while the West-Siberian has up to four beds, with average thickness being 2-20 m. The ore beds lie on the layers having some evidence of erosion. The beds themselves were subjected to partial denudation during sedimentation of overlying rocks.

The ores typically are composed of oölites of variable size having hydrohematite, hematite, leptochlorite or siderite composition. They also contain fragments of oölites and sandy-clayey material cemented by the same minerals which compose oölites. There are also lenses of siderite, and interlayers of enclosing sandy-clayey rocks.

The Ayat and West-Siberian basins have a characteristic change in the mineral composition of the ores in the direction from the former coastline towards the sea, hydrogoethite being gradually substituted by leptochlorites. Besides, in the Ayat deposit the later sideritization of hydrogoethite and leptochlorite ores takes place which, according to B. Krotov, is related to a regression of cretaceous sea and formation of closed lagoons.

Deposits of such a formation are known in other countries: the Lorraine basin of minette-like (fine oölite) ores. It has the area of 1 100 km^2 and is mainly located on the territory of France, partially in FRG, Belgium and Luxembourg. Similar deposits are well developed in China.

THE KERCH IRON ORE BASIN is characterized by two types of deposits of marine platform sedimentary oölite iron ores of the Kimmerian age. The first type of the deposits is confined to large tectonic brachy-synclinal structures, such as troughs, whereas the second type, singled out by E. Shnyukov, is related to pseudotectonic structures, such as compensation sags in the zones of mud volcanism, called "indented synclines".

In all troughs and sags the ore bed of the Middle Kimmerian age is underlain by the limestones of the Pontian suite, or by the clays of the Lower Kimmerian suite, and is overlain by the clays with an admixture of sandy and aleurolite material of the Upper Kimmerian suite. The thickness of the ore beds in the central parts of the deposits is 25-40 m, in the fringing parts it becomes somewhat lower down to 0.5 m (Fig. 8).

The main types of ores are "tobacco" and "brown". The first type dominates in oxidation-reduction zone, whereas the second was formed at the expense of the first type in an oxidation zone. Subordinate, less distributed are manganosiderite-rhodochrosite concretionary ores and manganese-ferruginous "spawn" ores which differ from the brown ores by higher manganese content.

The main minerals of the tobacco ores are hydroferrichlorite, ferrimontmorillonite and hydrogoethite (ochreous and dense varieties), as well as carbonates of the manganosi-

…erite-rhodochrosite series. In the fragments
… oölites one often finds quartz and feldspar.
Phosphates (vivianite and kerchenite),
…anganese hydrooxides (psilomelane,
……dite. pyrolusite), and pyrite are more
… observed. The findings of realgar are
…

…e main minerals of the brown ores are
… goethite and ferrimontmorillonite. Psi-
…ane. pyrolusite, gypsum, aragonite,
…ite. pyrite, kerchenite, quartz, feldspar
… glauconite are subordinate. Typical
…tures of the ores are oölitic and
… …tic. The brown ores contain (w.%): Fe
… MnO 3, V_2O_5 1.19, P 1.0, S 0.06, As
…

…e reserves of iron ores in the main
…sits of the Kerch basin are estimated as
… …n tons, including 560 mln tons of
… …n ores.

THE LORRAINE IRON ORE BASIN is located
… troughs. The ore-bearing sandy-
…onate strata have the thickness of
… …m and incorporate 4-12 ore beds of
… thickness from 1 to 6 m interbedded
… barren rocks of the same thickness. The
…bearing strata in the east of the basin
… ps out on the surface and subsides to the
… where it has been intersected by
… holes down to the depth of 800 m. It is
…derlain by sandstones and overlain by the
…rls of Jurassic age.

…e iron ores in the deposit have fine
… structure (0.25-1 mm in diameter) and
… composed of goethite, stilpnosiderite
…on oxide gel having an increased content
… phosphorus), ferruginous chlorites and
siderite. The ores contain (w.%): iron 31-36,
phosphorus 0.6-1.8, manganese 0.5, sulphur
0.01-0.4. The main commercial value is
attributed to a "grey bed" of 3-9 m thickness
which is well-developed in all troughs and
composed of ores with a carbonate
low-melting-point cement. The other beds
contain siliceous cement and ores with
a high-melting point. Total reserves of the
ores in the basin are estimated as 15 bln
tons.

SEDIMENTARY CONTINENTAL DEPOSITS

Hydrogoethite bean-oölite lacustrine-marsh
deposits are represented by a great number
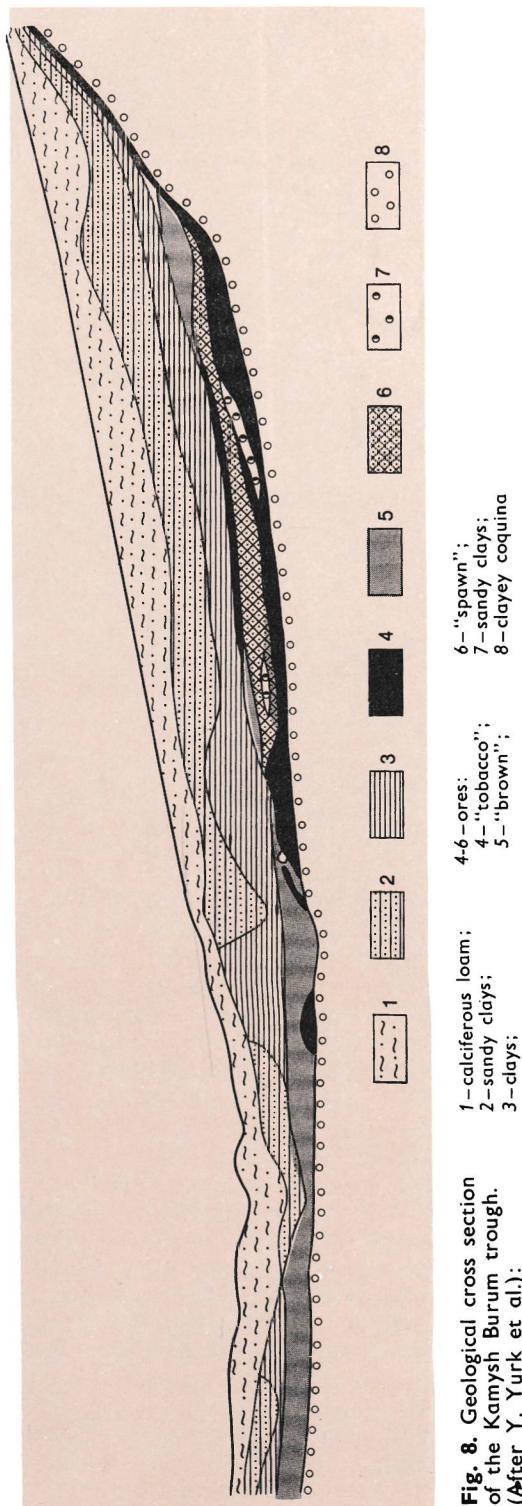
Fig. 8. Geological cross section of the Kamysh Burum trough. (After Y. Yurk et al.):

1—calciferous loam;
2—sandy clays;
3—clays;
4-6—ores:
4—"tobacco";
5—"brown";
6—"spawn";
7—sandy clays;
8—clayey coquina

of small occurrences, particularly on the Russian platform. Such ores are composed of accumulations of hydrogoethite geodes and oölites in clayey-sandy lacustrine-marsh sediments. Jurassic ores of such type are known in the Tula and Lipetsk regions, in the upper reaches of Vyatka, Kama and Sysola, as well as in the northern part of the Russian platform. They are of Quaternary age and continue their formation process even at the present time.

The ores have characteristically low content of iron (30-40%). At present, the deposits of such a formation have lost their commercial significance.

Siderite-leptochlorite-hydrogoethite deposits in ancient river sediments have come into the list of commercially important deposits of the Soviet Union after the discovery of the large Lisakovsk deposit in the Kustanai region. The deposits of this formation are related to channel, floodplain, and often estuarine sediments in Oligocene paleorivers of the Turgai depression and the Turan plate that penetrated marine sediments of the sedimentary cover of an Epipaleozoic platform. Sandy-clayey ore-bearing sediments lie on a denudated surface of marine Lower Oligocene clays and are overlain by pebble-clayey sediments of Middle and Upper Oligocene.

The ore beds are stretched over tens of kilometres along the channel of paleorivers and are represented by the main channel ore body and accompanied by floodplain bodies of lenticular, oval and irregular shapes.

The ores are made of hydrogoethite, leptochlorite, siderite, stilpnosiderite, quartz (fragmental), calcite, ankerite, clay minerals, pyrite, markisite, gypsum and, occasionally, of manganese hydroxides. Dominating ores are oölitic. Iron content in the ores is low (30-35%), but that of phosphorus is high (about 0.5%). Besides the Lisakovsk, in the Turgai depression deposits of a similar type, such as Oktyabrskii and Shiyelin are known.

In the North Aral sea region there are also the Taldy-Espe, Kok-Bulak, Taldy-Bulak deposits and a number of other smaller size deposits. The Kashkaratskii ore basin is located in the North East of Ustyurt Plateau.

METAMORPHOGENIC DEPOSITS

This series of deposits includes beds of ferruginous quartzites and rich metamorphic ores of ancient formations.

The deposits of ferruginous quartzites occur in metamorphosed sedimentary complexes of the Precambrian geosynclines of crystalline shields, as well as in folded basements of ancient platforms, or in the projecting uplifts of ancient structures in the cores of anticlinoria of younger folded regions. Ferruginous quartzites occur only within Precambrian folded areas. They, being mostly marine chemogenic sediments, are clearly identifiable among terrigenous and volcanogenic-sedimentary enclosing complexes, producing transitional chemogenic-terrigenous, chemogenic-terrigenous-carbonate and chemogenic-volcanogenic varieties primarily in the lateral parts of the ore beds.

In the Soviet Union ferruginous quartzites are known in the Kola peninsula and Karelia (Olenegorsk, Kirovogorsk, Kostamuksha, Mezhozyorsk and other deposits), in the KMA basin (Korobkovsk, Lebedinsk, Stoilensk, Saltykovsk, Oskolets, Mikhailovsk and other deposits), in the Krivoi Rog-Kremenchug iron ore basin (Skelevatka, Ingulets, Novo-Krivoirogian, Bolshaya Gleevatka, Pervomaisk, Gorishne-Plavninsk and other deposits), in Kazakhstan (Karsakpai group of deposits), in the Soviet Far East (Lesser Khingan and Ussuri groups of deposits). There have been also revealed, though not adequately studied, ferruginous quartzite deposits in Tuva (Mugur), in the South Urals (Taratash) and in the Southern Yakutia in the BAM region (Baikal-Amur Railroad Line) (Charo-Tokko deposit).

In other countries large areas of ferruginous quartzites are also known, such as iron ore belt in Labrador (Canada), a large group of deposits in the area of the Lake Superior (USA), in the state of Minas Gerais (Brazil), in the states of Bihar and Orissa (India), in the Nimba Mts region (Liberia and Guinea) and Tamazimbi (South African Republic), in Hamersley (Western Australia), as well as the deposits of the Anshan group and others in the north of China, the Musan deposit in

the Korean People's Democratic Republic and in a number of other regions of the world.

All the largest deposits of ferruginous quartzites with total reserves of ore estimated in billions and tens of billions of tons are related to Lower Proterozoic eugeosynclinal formations that went through metamorphism of greenschist facies. The main minerals of the ferruginous quartzites in this formation are quartz, magnetite, hematite, cummingtonite, biotite, chlorite, occasionally siderite, and alkaline amphiboles and pyroxenes. The texture of the quartzites is mainly fine-grained, rarely medium-grained, while the structure could be bedded and plicated. The deposits of this formation occur in sedimentary and partially in volcanogenic-sedimentary rocks. They are identified as the Krivoirogian type or the Lake Superior type of deposit.

The Lower Proterozoic deposits of amphibolite facies that went through more intensive metamorphism are represented by smaller size deposits (hundreds of millions of tons), such as Olenegorsk, Kostamuksha and others. The main minerals of the ferruginous quartzites of the amphibolite formation are quartz, magnetite, hematite, hornblende, hedenbergite, and diopside. The texture of the quartzites can be medium-grained, the structure being bedded, in places indistinctly bedded. The deposits of this formation occur in the metamorphosed sedimentary-volcanogenic rocks and are referred to the so-called Keewatin type, the name carried by the iron ore formation in Canada.

The most deeply metamorphosed Archean deposits of granulite facies compose small size (tens-the first hundreds of millions of tons) deposits (Mariupol, Taratash, and others). The main minerals of the quartzites in the granulite formation are quartz, magnetite, hypersthene, actinolite, talc, cummingtonite. The texture of the quartzites is coarse-grained, the structure being bedded and indistinctly bedded. The host rocks are represented by metamorphosed sedimentary and volcanogenic-sedimentary formations.

Ferruginous quartzites typically contain iron within the limits of 20-40%, most often the content is 32-37%. Ferruginous quartzites

have low content of phosphorus and sulphur, and if magnetite dominates over other ore-bearing minerals they are easily beneficiated. High-grade iron ores appear to be a product of natural enrichment of ferruginous quartzites as a result of quartz leaching and decomposition of silicates in the processes of ancient weathering or metamorphism.

Two basic morphologic types of ore bodies which contain high-grade iron ores can be identified, i.e. mantle-shaped and linear. Mantle-shaped deposits occur over steeply inclined beds of ferruginous quartzites forming flat-lying ore beds of considerable area which have a pocket-shaped footwall and are classified as typical weathering crust deposits. Linear ore bodies look like wedge-shaped high-grade ore zones having considerable strikewise length and thickness and dipping to a depth in ferruginous quartzites. They were formed in the zones of faults, fissuring, crushing, crumpling, and bending in the processes of metamorphism. Some deposits were supposedly formed as products of the Precambrian weathering crust and were later subjected to metamorphism and secondary weathering during the post-Precambrian time.

The minerals of high-grade ores, related to weathering, are represented by martite and martitized magnetite, hematite as a relict mineral of ferruginous quartzites, and as a dispersed mineral; goethite and hydrogoethite, clay minerals. The secondary minerals are pyrite and carbonates. The ores have characteristically high content of iron (54-69%) and low contents of sulphur and phosphorus.

Metamorphic bodies of high-grade ores are composed of magnetite and magnetite-specularite ores that occur in ferruginous quartzites, metamorphic sedimentary and volcanogenic-sedimentary rocks, such as amphibole, magnetite-amphibole, quartz-biotite and other schists. The ore bodies could be sheet-like, lenticular and pillar-shaped. In some cases they are stock- or nest-shaped. Typically they have steep dipping and are localized in crush zones, as well as in bends or limbs of synclinal folds.

The ores are mainly composed of magnetite, hematite (in a form of iron glance),

alkaline amphiboles (rhoducite, riebeckite and others). Magnesian ferruginous amphiboles of cummingtonite-grunerite composition, aegirine, quartz, albite and carbonates are referred to as subordinates. Amphibole-magnetite, amphibole-magnetite-specularite, quartz-magnetite-specularite, aegirine-amphibole-magnetite and carbonate-magnetite-specularite ores are distinguished, depending on the principal minerals composing the ore.

In accordance with the modern understanding (Ya. Belevtsev et al), metamorphic deposits of high-grade ores were formed as a result of an endogenous magnesian-iron metasomatism of Precambrian sedimentary and volcanogenic-sedimentary rocks under the action of hydrothermal metamorphic solutions which are generated during metamorphism of the rocks containing hydroxyl-bearing and ferruginous silicate minerals.

The Pervomaisk and Zheltorechensk deposits in the northern part of the Krivoi Rog basin can serve as characteristic examples of metamorphic deposits.

THE KRIVOI ROG IRON ORE BASIN is located on the right bank of the Dnieper river, along the lower reaches of the Ingulets river and its Saksagan and Zheltaya tributaries. It is stretching north-north-east over 100 km (Fig. 9).

The territory of the basin comes as a part of the Ukrainian crystalline massif and appears to be a part of the Precambrian eugeosyncline. Its Archean strata are composed of gneiss, granites, migmatites, amphibolites, and crystalline schists that are located west and east of the Krivoi Rog basin.

The overlying sequence is composed of the Proterozoic Krivoi Rog geosynclinal

Fig. 9. Structural scheme of the Krivoi Rog basin. (After Ya. Belevtsev):

1 – Saksaganian plagiogranites;
2 – migmatites;
3 – metabasites;
4-6 – the Krivoirogian series:
    4 – lower suite;
    5 – middle suite;
    6 – upper suite;
7 – microcline granites;
8 – axes of tectonic faults;
9 – large synclines;
10 – large anticlines
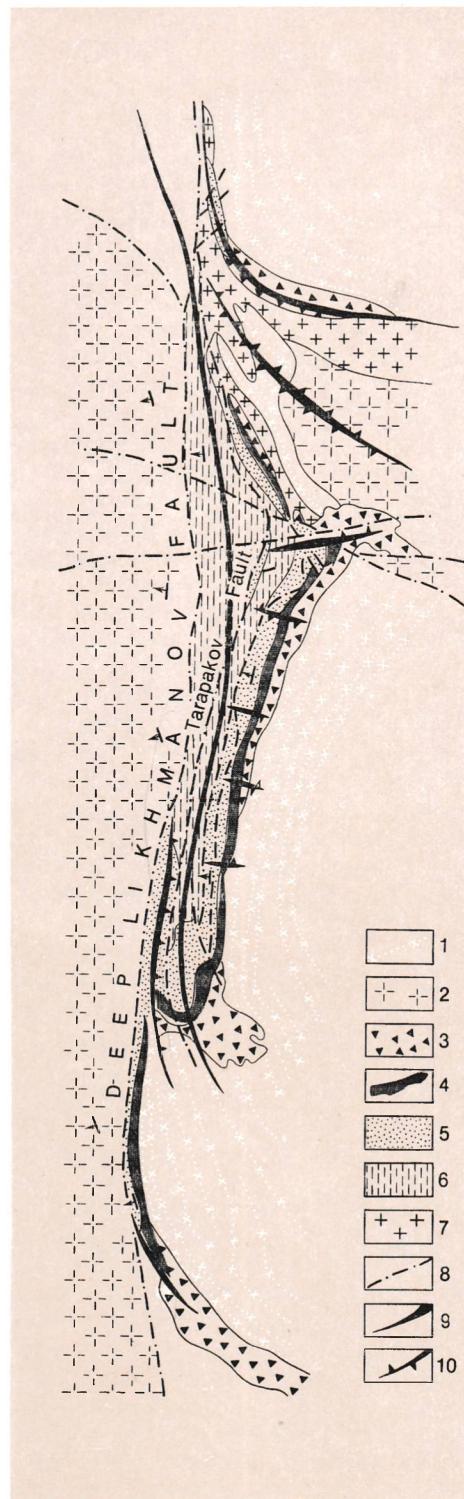
series which is subdivided into three divisions: lower, consisting of green schists with arkoses, quartzites and phyllites; middle, consisting of ore itself, ferruginous-quartzites and schists; and upper, consisting of quartzite-sandstone-schists with lenses of marmorized limestones.

A complete profile of the middle division has the thickness up to 1 300 m and includes nine beds of ferruginous quartzites that are marked with indices K_2^{1f}-K_2^{9f}. These beds have interlayers of quartz-sericite, chlorite-sericite and other schists and micro-quartzites.

The Krivoi Rog suite makes a complicated synclinorium consisting of synclinal and anticlinal folds with the limbs dipping at an angle 45-80°. The synclines typically have keel-shaped closure (Fig. 10). The lower bends of the synclines subside at an angle up to 40° northward. Usually, the limbs of the folds are cut off by longitudinal faults, the largest of which being the Saksagan thrust. As a result of such dislocations, the following ore-bearing structures could be delineated (from south to north) over the whole stretch of the basin: Ingulets (the southern ore field), Saksagan (the Main, or Saksagan ore field), Per-vomaisk, Annovsk, Zheltorechensk (the Northern ore field), and Popelnastovsk. In the Northern ore field sedimentary rocks are intruded by Proterozoic granites.

Among ferruginous quartzites one can identify magnetite, magnetite-hematite, hematite types and their oxidized varieties. Non-oxidized magnetite and magnetite-hematite varieties are of the main importance. High-grade ores, that mainly consist of oxides and hydrooxides of iron, make up sheet-, pillar- and stock-like or lenticular ore bodies among ferruginous quartzites. The ore bodies are located within the beds of ferruginous quartzites and form groups and chains with variable intervals between them. Individual ore bodies may merge at depth forming large ore shoots often with keel-shaped foot and the same strike and dip as the lower bends of the folds. In some localities of Saksagan and Zheltorechensk districts high-grade ores, having bed-like configuration, occur in the zone of stratigraphic unconformity between
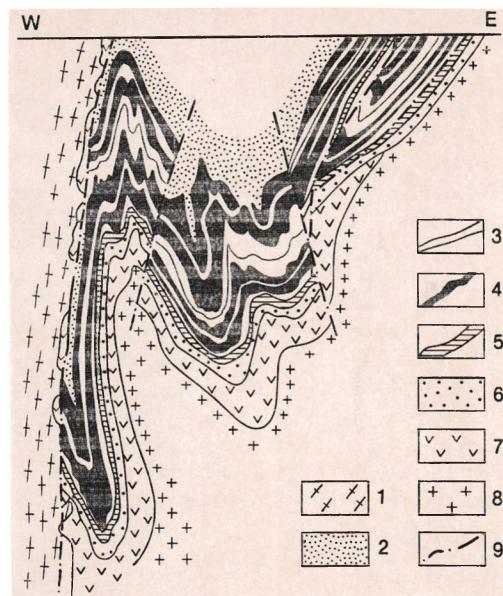
Fig. 10. Geological cross section of the Krivoirogian basin nearby Krivoi Rog city. (After Ya. Belevtsev):

1 – microcline granites;
2 – upper suite quartzites;
3 – middle suite schists;
4 – middle suite ferruginous quartzites;
5 – talc-carbonate horizon;
6 – lower suite quartzites;
7 – albitophyres;   8 – plagiogranites;
9 – faults

the sediments of the middle and upper divisions of the Krivoi Rog series.

In the Northern ore field silicate-magnetite and silicate-magnetite-specularite ores are developed. They occur both in conformity with substituted rocks, and in disconformity, crosscutting bedding and foliation of the latter. The ore bodies are controlled by the zones of crushing, crumpling, tectonic seams and nodes of faults.

Four basic types can be distinguished among high-grade ores of the Krivoi Rog basin. They are: (1) martite and hematite-martite (local name is "blue"); (2) martite-hematite - dispersed-hematite-hydrogoethite ("blue paint"); (3) hematite-dispersed-hematite-hydrogoethite ("paint"); (4) magnetite and magnetite-specularite. The ores of the first type, besides martite and relict hematite, contain small quantities of relict magnetite, dispersed hematite, chlorite,

Fig. 11. Schematic map of the anomalous gravity field of the Kursk Magnetic Anomaly. (After N. Schmidt):

1-4 – gravitational anomalies:
    positive (*1*); negative with small (*2*);

intermediate (*3*) and high (*4*) intensity;
5 – ferruginous quartzites

sericite, pyrite, carbonates, clay minerals, quartz and apatite. The ores of the second type, besides the main minerals, contain sericite, quartz, clay minerals, alunite and sphene. The ores of the third type, besides the main minerals, contain kaolinite, clay minerals, chlorite and carbonates. The ores of the fourth type, besides dominating magnetite and specularite, contain amphibole (cummingtonite, grunerite, riebeckite), aegirine, biotite, albite, quartz, carbonates, chlorite, pyrite, pyrrhotite and chalcopyrite.

High-grade iron ores in the Krivoi Rog basin are characterized by high content of iron (54-64%) and low content of harmful admixtures (sulphur 0.03-0.15%, phosphorus 0.04-0.26%).

The reserves of high-grade ores in the basin are estimated as 1.5 billion tons with 57.6% average content of iron, and that of ferruginous quartzites as 18 billion tons with 35.9% average iron content.

THE IRON ORE BASIN OF THE KURSK MAGNETIC ANOMALY (KMA) has the area of 70000 km² and incorporates four iron ore regions, i.e. Belgorod, Novy Oskol, Stary Oskol and Kursk-Orel. Two commercial types of ores occur here: sedimentary-metamorphosed ferruginous quartzites and high-grade iron ores of the weathering crust of ferruginous quartzites.

The ferruginous quartzites take part in the structure of the crystalline basement making up the largest part of the middle suite in the Kursk series of Lower Proterozoic. Due to a very complicated folded structure and due to Pre-Paleozoic erosion, ferruginous quartzites are overlain by sedimentary rocks of the Devonian, Jurassic, Cretaceous and Quaternary ages. They possess pronounced magnetic properties and heightened density which makes it possible to map their distribution reliably using magnetic and gravimetric surveying. Such works have established that ferruginous quartzites in KMA are basically confined to two iron ore belts of the north-western strike (Fig. 11). Inside each belt the ferruginous quartzites occur in the form of one or several parallel, occasionally intermittent, beds that have the steep dip (70-80°) and almost uniform northwest strike. In the hinges of large fold structures complicated by the series of very flattened out supplementary folds, large massifs of ferruginous quartzites of a few
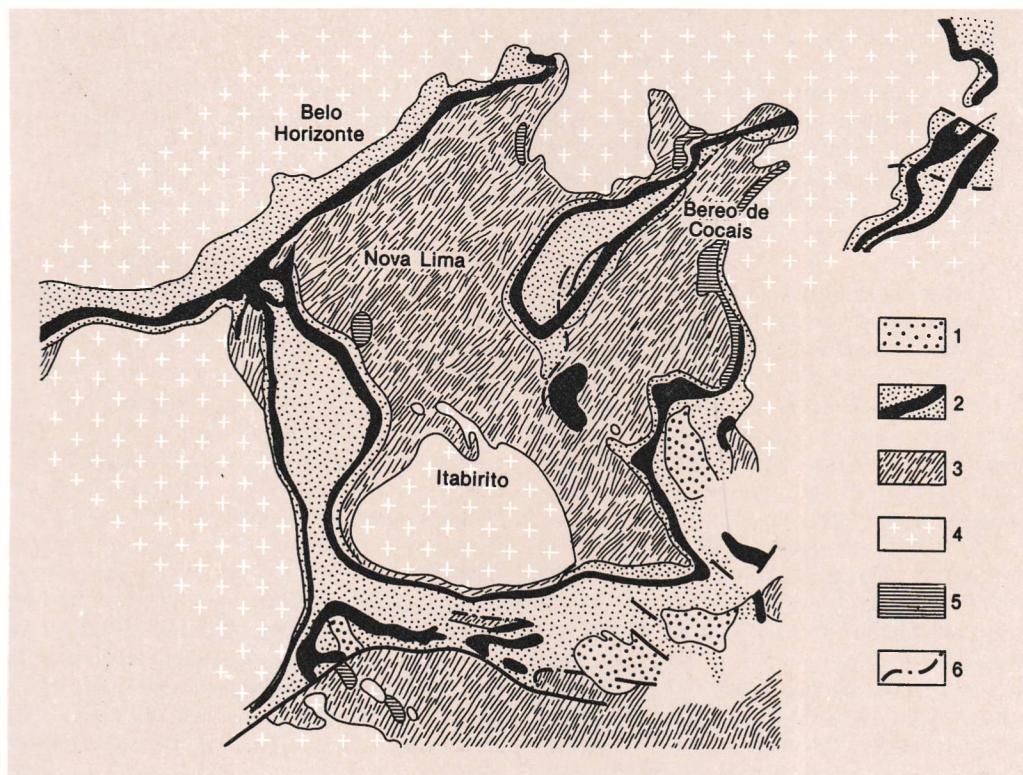

Fig. 12. Schematic geological map of the "iron ore quadrangle" (Minas Gerais, Brazil). (After Ch. Park):

1 – quartzites, sandstones, conglomerates and limestones;
2 – ferruginous quartzites, phyllites, schists, extrusives and tuffs;
3 – quartz-micaceous schists, gneiss, greywacke, tuff and diabase;
4 – granites;
5 – basic and ultrabasic rocks;
6 – faults

kilometres wide were formed. Such structures as Mikhailovsk, Lebedinsk, Stoilensk, Pogrametsk and others are confined to the largest deposits of ferruginous quartzites. On the erosion surface such massifs compose continuous fields of ferruginous quartzites containing large deposits of high-grade iron ores of weathering crust.

Ferruginous quartzites in terms of mineral composition can be identified as magnetite, hematite-magnetite and hematite (specularite). They are represented mainly by thin-laminated, fine and very fine-grained rocks. The main ore minerals in the quartzites are magnetite (5-30%), hematite (55-5%), quartz (30-60%). There are also subordinate quantities of silicates (such as actinolite, tremolite, alkaline amphiboles of the rhoducite-riebeckite series, aegirine, pargasite, biotite, talc, garnet and others), and carbonates (dolomite and calcite). The accessory minerals are apatite, tourmaline, zircon, rutile, pyrite and pyrrhotite. The structure of the quartzites in magnetite interlayers is crystalloblastic, in hematite interlayers it is lepidoblastic, and in quartz interlayers it is hornfels-like. Average content of iron in ferruginous quartzites is 32-36%.

High-grade martite and specularite-martite iron ores of weathering crust, composed of martite, specularite, thin-flaky hematite, iron hydrooxides and chlorite often inherit the thin-laminated structure of ferruginous quartzites. They are characterized by very high content of iron (64-69%) and negligibly small content of harmful admixtures (hundredths of per cent).

The discovered and potential reserves in the Kursk Magnetic Anomaly up to the depth of 600 m are estimated as 100 billion tons, including 6 billion tons of high-grade iron ore.

THE IRON-ORE BASIN IN THE STATE OF MINAS GERAIS has the area of 7 thousand km² and is located in the "iron ore quadrangle" in the central part of Brazil (Fig. 12).

The Archean crystalline schists and gneisses in this area are unconformably overlain by Lower Proterozoic rocks of the Minas series having the thickness up to 7 km. They are composed of quartzites, schists, fillites, conglomerates, metamor-phosed lavas and tuffs. The middle suite of the Minas series is represented by thin-bedded and massive hematite ores, and by martite-magnetite quartzites with the interlayers and lenses of manganese ores interbedded with dolomites, quartzites etc.

The hematite ores and quartzites stretch from east to west over 150 km, and from north to south over more than 75 km. The thickness of the structures varies from a few tens of metres to 1 km (average thickness being 150 m). Their structure is thin-banded with crosswise dimensions of the bands from 1 mm to 2 cm. Their texture is very fine- and fine-grained with the grain size of iron ore minerals ranging from 0.001 to 0.4 mm. Iron content in the high-grade ores is 63-69%. The reserves are estimated as 30 billion tons.

THE IRON-ORE BASIN OF HAMERSLEY is located in the Western Australia. Its area is 150 000 km², the length being around 600 km and the width 350 km (Fig. 13). The Archean granite-gneiss is unconformably overlain by Lower Proterozoic rocks that can be subdivided into three suites. The lower suite is represented by basalts, arkose sandstones and shales. The middle suite (Hamersley) of 2.5-km thickness is represented by hematite ores and quartzites, siliceous schists, dolomites, aleurolites, dolerites and dacites. The upper suite is represented by terrigenous quartz rich of fragmental rocks, having the interlayers of dolomites and ferruginous quartzites. The rocks are gently steeping in the central part of the basin whereas the peripheral parts of the basin are folded and cut by faults. The Hamersley suite contains three groups of hematite ore beds, quartzites and schists having thicknesses of 200, 650 and 200 m, respectively, counting upwards. The types of the ores are: massive hematite, hematite conglomerates and limonite pisolitic. Iron content in ferruginous quartzites is 25-40%, that in high-grade ores (blue hematite) being 64-67%. The content of phosphorus and sulphur is hundredths of per cent, that of silica being up to 3.6%. There are only over 100 deposits in the region. The total reserves of high-grade ores in the basin are estimated as 32 billion tons. Ferruginous quartzite reserves reach hundreds of billions of tons.
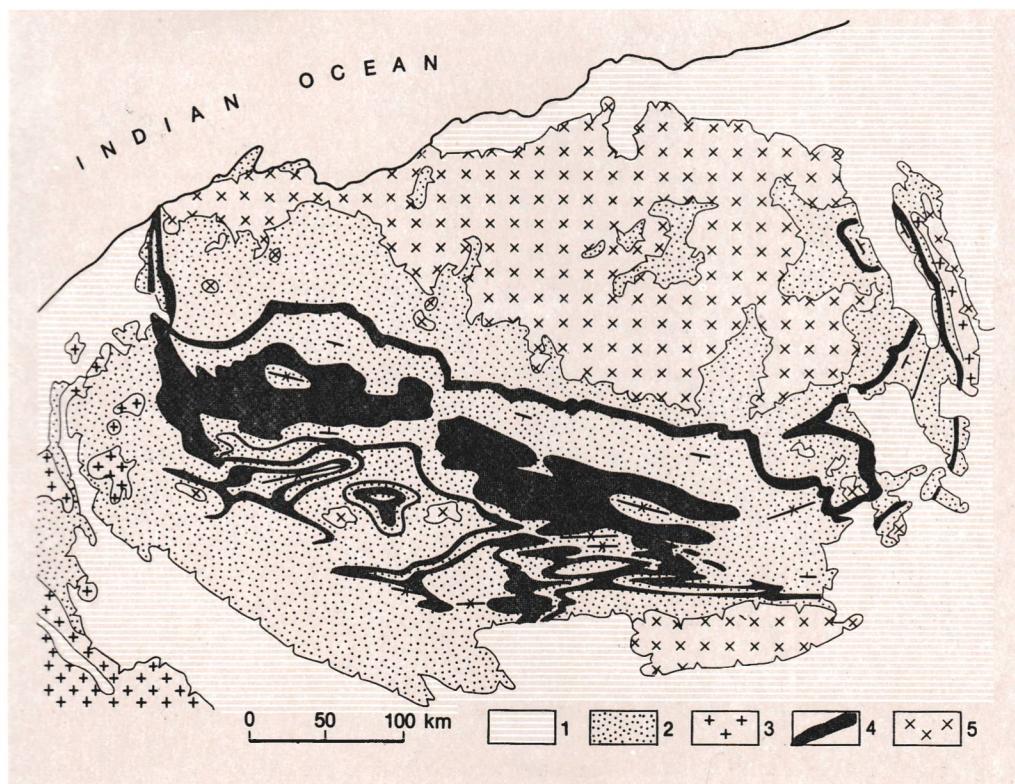
Fig. 13. Geological structure of the Hamersley iron ore basin (West Australia). (After T. Trendull):

1 – Phanerozoic sedimentation rocks of the platform cover, rocks of the Upper and Middle Proterozoic;
2 – sedimentary rocks of the Low Proterozoic;

3 – granites:
4 – ferruginous quartzites of the Low Proterozoic;
5 – Archean granite-gneiss

IRON-ORE BASIN IN THE LAKE SUPERIOR REGION. The Archean granites and gneiss are overlain there by the Lower Proterozoic rocks represented at the base by quartzites, conglomerates, dolomites, schists, in the middle part of the profile by ferruginous quartzites, schists and barren quartzites and in the topmost part of the structure by sandstones and ferromagnesian lava sheets.

The ferruginous quartzites in the largest deposit of the area, called Mesabi (Fig. 14), stretch strikewise over 145 km having the width of 3-16 km. They include four productive levels of the total thickness over 200 m. Iron content in the magnetite quartzites is 25-38%. High-grade massive ores of shoot-like and lenticular bodies are traced down to the depth of 800-1 200 m. The ores are represented by quartz-hematite, rarely by quartz-magnetite, martite and

hematite varieties. The high-grade ores contain 50-62% of iron, the contents of sulphur and phosphorus being from hundredth of percent up to 0.1%. The reserves are estimated as 2 billion tons, those of ferruginous quartzites 40 billion tons.

2 MANGANESE DEPOSITS

Manganese ores first began to be used late in the 18th century to make paints and medicines. They found wide application in the second half of the 19th century after the new methods of steel production had been discovered. At present metallurgical industry appears to be the main consumer of manganese. Only 5% of manganese in the world is used in electrical (to manufacture dry batteries), chemical (paint and varnish production), and ceramic industries.
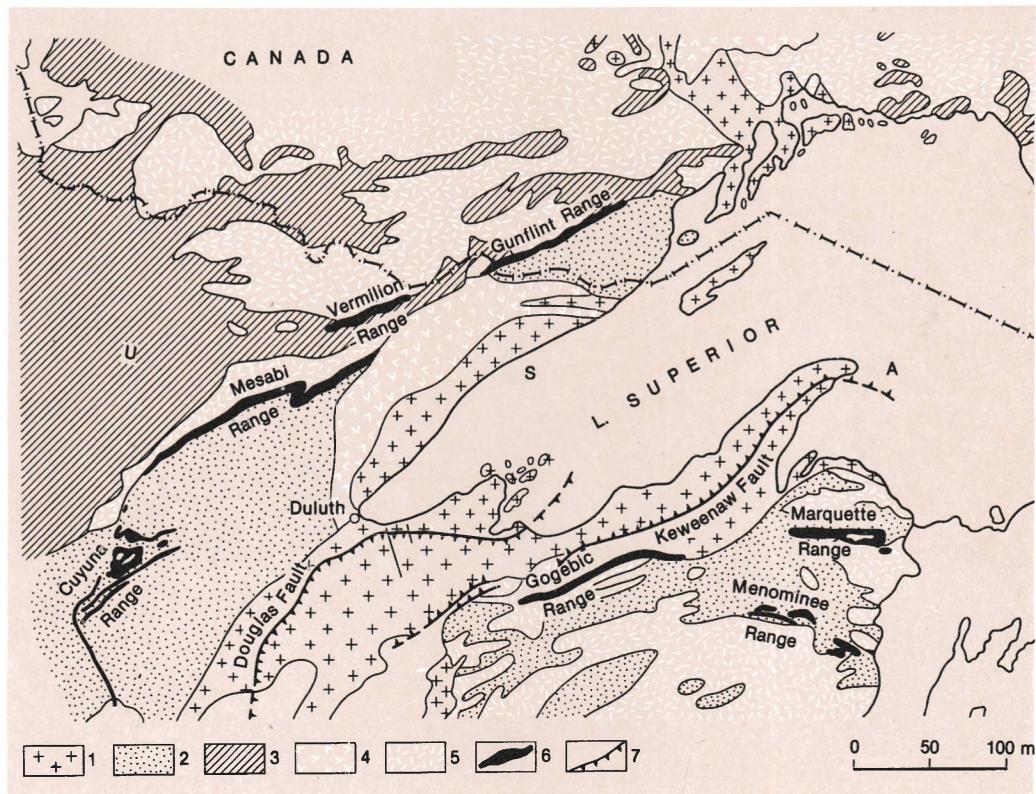
Fig. 14. Geological struture of the Lake Superior basin. (After S. Goldich):

1 – sandstones, clayey shales and Upper Proterozoic
    volcanics;
2 – argillites and Middle Proterozoic ferruginous
    quartzites;
3 – crystalline schists and Low Proterozoic
    amphibolites;
4 – gabbro;
5 – granites;
6 – ferruginous quartzites;
7 – faults

Additions of manganese to iron and steel substantially increase their toughness, malleability and hardness. Manganese is introduced into a melt in the form of ferromanganese (70-80% of Mn, 0.5-1% of C, the remaining is Fe). In nonferrous metallurgy manganese is used to produce manganese-containing bronze, brass and other alloys with nonferrous metals. In this way, their strength is improved and corrosive resistance is gained.

The total world reserves of manganese ores are estimated to be 3.1 billion tons, including 2.4 billion tons in the USSR, from 200 to 50 million tons in Gabon, Australia, Brazil, India and South African Republic. Potential reserves of the South African Republic are estimated as 3 billion tons.

Production of manganese ore in 1915 was 1.5 million tons. In 1975 it reached 22 million tons. At present, manganese ore is produced in 30 countries of the world. Over half of the total production is made by the USSR, from 5 to 1.5 million tons of manganese ore a year is produced by the South African Republic, Brazil, Gabon, Australia, and India. The price of the ore, containing 40-50% of manganese and less than 0.14% of phosphorus is 70 US dollars per ton.

Deposits of manganese ores which have the reserves of over one billion tons are regarded as unique. Large deposits have hundreds of millions of tons, and small-size deposits contain tens of millions of tons. The ores containing 30-36% of manganese

and less than 0.2% of phosphorus are used in metallurgical production. In easily beneficiated ores commercial content of manganese is over 10%, that for hardly beneficiated ores is over 20%, the content of phosphorus being not more than 0.015% of manganese.

GEOCHEMISTRY AND MINERALOGY

Manganese has one isotope ^{55}Mn. The clarke of manganese is 0.1%. An increase of manganese content (up to 1.5 clarke) is observed in ultrabasic and basic rocks. The clarke of concentration for manganese is high (about 300).

Manganese has two stable valencies. Mn^{2+} and Fe^{2+} compounds substitute each other in endogenous processes, whereas Mn^{4+} and Fe^{3+} are isomorphous in exogenous processes. The latter precipitate at different values of pH, i.e. iron precipitates under more oxidizing conditions in comparison to manganese which precipitates in less oxidized substance (farther from the coast) (Fig. 15).

Endogenous accumulations of manganese have no commercial value. Unique and large deposits of manganese are known in sedimentary rocks, large and small-size deposits occur in volcanogenic-sedimentary rocks and in weathering crusts of metamorphic rocks.

Over 150 minerals containing manganese are known. Commercial value minerals (Mn, %) are: pyrolusite MnO_2 (55-63), braunite Mn_2O_3 (60-69), hausmannite $Mn \cdot Mn_2O_4$ (65-72), manganite MnOOH (50-62), vernadite $MnO_2 \cdot nH_2O$ (40-45), psilomelane $MnO \cdot MnO_2 \cdot nH_2O$ (40-60), rhodochrosite $MnCO_3$ (40-45), manganocalcite $(Ca, Mn)CO_3$ (7-23) and manganosiderite $(Mn, Fe)CO_3$ (23-32).

METALLOGENY

During geosynclinal cycle the main concentration of manganese occurred at an early stage, when sedimentary ores were accumulated in the coastal parts of geosynclinal basins. The middle and late
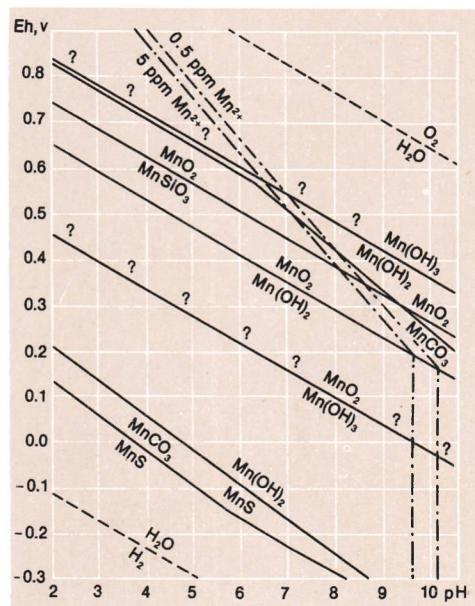
Fig. 15. Fields of stability of heteroaged manganese oxides, hydroxides, carbonates and silicates depending on acidity-alkalinity (pH) and redox (Eh) conditions. (After R. Garrels)

stages of the geosynclinal cycle for manganese are considered as non-productive. During the platform stage manganese deposits of sedimentary and weathering groups were formed.

In the Archean-Proterozoic metallogenic epoch large geosynclinal structures were formed, which in a number of cases contained highly productive manganiferous strata (such as gondites in Madhya Pradesh, India and Neuta Dagvin in Ghana, ferruginous quartzites in the state of Minas Gerais, Brazil, etc.). Deposits of high-grade manganese ores were formed in the weathering crusts of these rocks at later epochs.

The Paleozoic epoch was characterized by manganese accumulations in the Lower Cambrian and Devonian rocks in relation to andesite-basalt volcanism (the deposits in the Urals, Central Kazakhstan, Kuznetsk Alatau, Uda-Shantar region of the Khabarovsk Krai of the USSR).

In the Mesozoic epoch manganese ores were formed in relation to the Upper Cretaceous (Transcaucasus, Trans-Baikal in
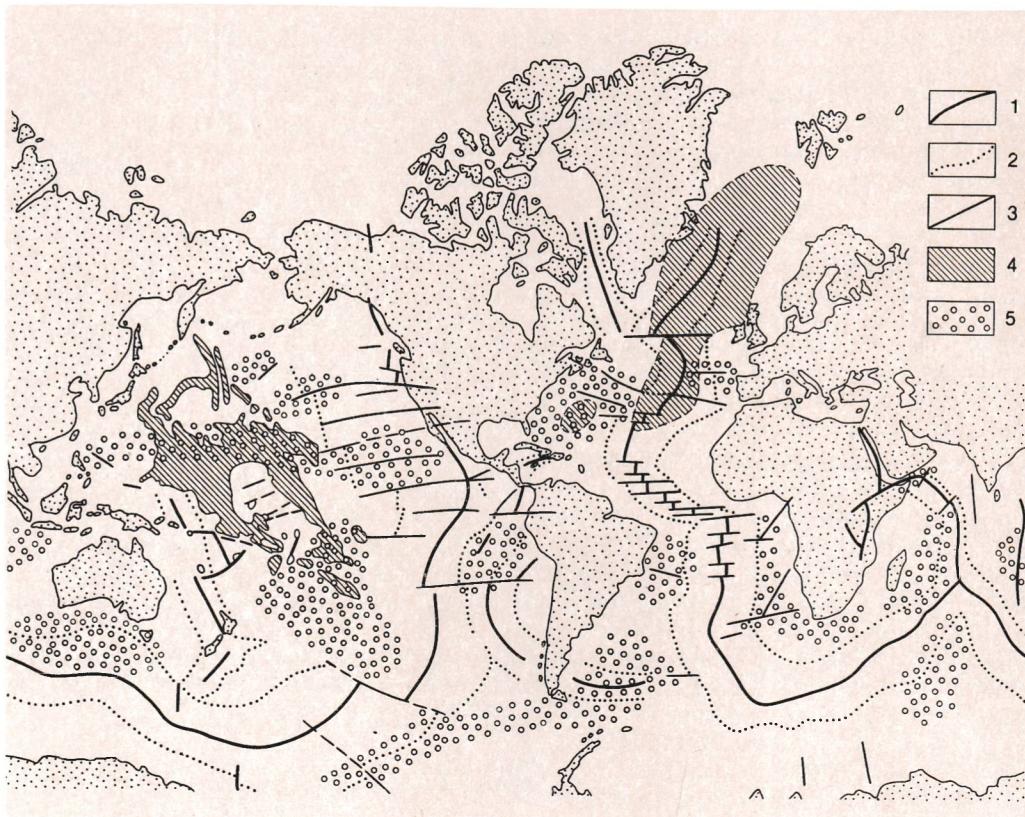
Fig. 16. The main geological structures of the World Ocean floor and distribution areas of iron-manganese nodules. (After V. Smirnov):

1 – axes of the middle-oceanic ridges;
2 – margins of ridges;
3 – transform faults;

4 – distribution areas of oceanic basalts;
5 – distribution areas of iron-manganese nodules

the USSR, the Sredna Gora range in Bulgaria), and Jurassic (coastal ridges of North America, New Zealand) volcanism.

The Paleogene epoch is distinguished by unique accumulations of sedimentary Oligocene manganese ores in the Southern border of the East-European platform (Nikopol basin, Chiatura, Mangyshlak and other deposits) and large accumulations of Paleocene manganese ores along the eastern slope of the Urals.

TYPES OF COMMERCIAL DEPOSITS

Commercial types of manganese deposits are represented by (1) sedimentary; (2) volcanogenic-sedimentary; (3) weathering; and (4) metamorphic ones.

SEDIMENTARY DEPOSITS

The rhodochrosite-psilomelane-pyrolusite deposits among the coastal-marine and lagoon Oligocene sediments are concentrated within the southern portion of the Paratetis, where Nikopol manganese basin, Chiatura and Mangyshlak deposits of the USSR and the Obrochishte deposit in Bulgaria were formed. These deposits contain over 70% of the world known reserves of manganese ores. Their origin is regarded by some geologists (such as A. Betekhtin, N. Strakhov, G. Avaliani, et al) as a sedimentary process, while others (such as G. Dzotsenidze et al) associate them with volcanogenic-sedimentary processes.

Huge amount of manganese ores is concentrated in iron-manganese concretions

nodules) that cover large areas of the bottom of Pacific, Atlantic and Indian oceans (Fig. 16). Their reserves are believed to be $2.5 \cdot 10^{12}$ tons, which is hundreds of times greater than total reserves known in all available deposits on the Earth. The oceanic reserves of these ores annually grow by 10 million tons, because concretions are continually formed at the ocean floor. Some geologists consider the bottom volcanic exhalations as the source of iron, manganese and other associated elements, such as cobalt, nickel, copper, zinc, lead, gold and silver. The others believe that the leaching of metals by oceanic water from the bottom basalts is the main reason, while the third group of geologists attribute the sources to the washout from the continents.

NIKOPOL BASIN. This manganese basin consists of the Nikopol and Bolshoy Tokmak deposits and includes a number of ore-bearing areas that stretch along the shores of Dnieper and Ingulets rivers in the area of Nikopol and Zaporozhye, forming a belt of 250-km length and up to 5-km width (Fig. 17). The bed of manganese ore lies in the Lower Oligocene sandy-clayey sediments that strike along the southern slope of the Ukrainian crystalline shield and the western slope of the Azov crystalline massif.

The ore bed of the thickness varying from a few centimetres to 4.5 m (in average 2-3.5 m), which is characterized by alternations of manganese concretions, lenses and nodules with sandy-aleurite-clayey sediments, lies almost horizontally, in places with south dipping at the angles from 5 to 7 degrees. The amount of manganese ores contained in the clayey-aleurolite barren mass reaches 50% by weight, average content of manganese being 15-25%. At the base of the ore bed a layer of 0.2 to 1.5-m glauconite sand thickness often develops.

Manganese ore sediments lie on the eroded surface over the Upper Eocene rocks
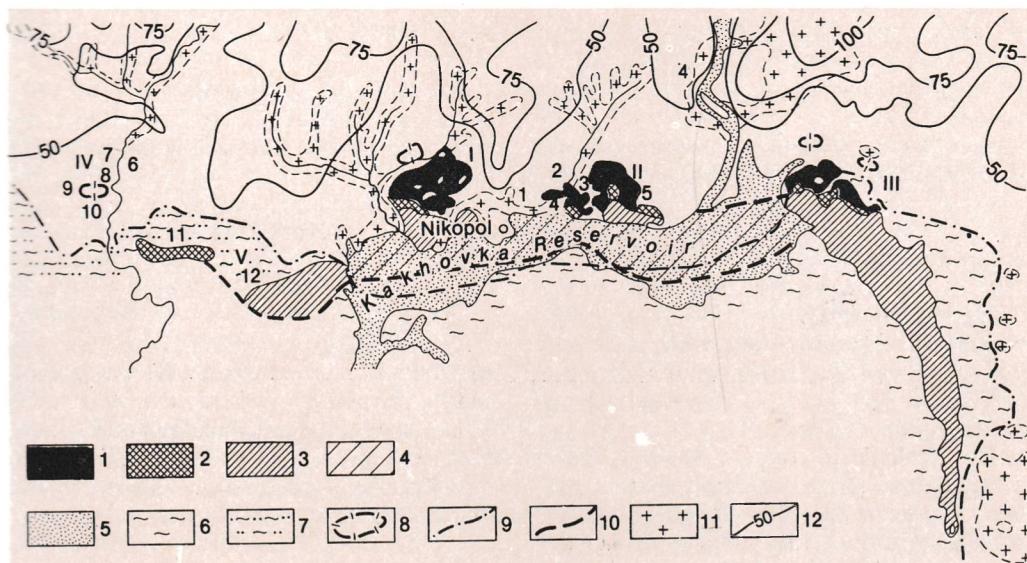
Fig. 17. Schematic map of the manganese ore locations in Nikopol basin. (After V. Gryaznov):

1-3 — manganese ores:
  1 — oxides;
  2 — oxides and carbonates;
  3 — carbonates;
  4 — areas where carbonate ores were destroyed by erosion;
  5 — Dnieper floodplain;
  6 — Oligocene clays;
  7 — Oligocene sandy clays;
  8 — "islets" of the Oligocene sediments;
  9 — boundary of the Oligocene sediments;
10 — assumed southern boundary of carbonate ores;
11 — outcrops of crystalline rocks;
12 — isohypses of the surface of the Precambrian rocks.
  Ore productive areas:
  I — West Nikopol;
  II — East Nikopol;
  III — Great Tokmak;
  IV — Krivoirogian;
  V — Dnieper-Inguletz interfluve. Arabic numbers on the diagram denote ore-productive sectors

composed of aleurolites, coaly clays and sands, or over the crystalline rocks of the basement, i.e. plagiogranites, migmatites and their weathering crusts. The overlying sediments are represented by Pliocene clays, shell-limestones, marls and Quaternary loams, having the total thickness of 15-80 m.

Post-Miocene erosion substantially changed an initial pattern of the manganese ore sediment distribution. At present, large areas of manganese ores are only found in the depressions of the crystalline basement.

Within the belt of the deposits, three main ore subzones are identified along with the subsidence of the crystalline basement. They are represented by oxide, mixed (oxide-carbonate) and carbonate manganese ore formations. The ratio of oxide, mixed and carbonate varieties in the prospected ores of these deposits is 25 : 5 : 70. The oxide ores are composed of pyrolusite, psilomelane, and manganite. The carbonate ores are primarily made of manganocalcite and an insignificant amount of rhodochrosite. The carbonate ores occur in the lower part of the ore bed, are found in the form of relics in the oxide ores, or form the layers composed completely of manganocalcite with the inclusions (up to 25%) of sandy-aleurite particles, shell fragments and phosphatized remnants of fish.

CHIATURA DEPOSIT. This deposit is located in Western Georgia, USSR, 140 km off the port of Poti. The area of the deposit is a high-altitude plateau of 600-800-m height which is cross-cut by the Kvirila river valley and its tributaries down to the depth of 150-250 m. Half of the ore-bearing area was destroyed by erosion.

The geological structure of the area is composed of granitoids, gabbroids, crystalline Precambrian and Lower Paleozoic schists, sandstones, Lias limestones, Bajocian quartz porphyries, carbonate terrigenous sediments of Cretaceous age and Tertiary sandy-clayey sediments. The manganese ore horizon, which stratigraphically corresponds to the lower layers of Oligocene, transgressively overlies Upper Cretaceous limestones, dipping east at the angle no more than a few degrees. On the south-western boundary the deposit is cut by a large fault having north-west strike.

The Oligocene sediments are distinguished as under-ore, the ore horizon and over-ore sediments. At the base of the under-ore sediments a basal conglomerate of 0.5-m thickness occurs being overlain by quartz-arcose and micaceous sandstones of 30-m thickness.

The manganese ore horizon is represented by interbedding of ore layers and opoka-like sands and clays (Fig. 18). The number of the beds varies from 3 to 25, their thickness being 1-50 cm. The thickness of barren beds may reach 1 m. The total thickness of the ore horizon is 14 m, being in average 4.2 m. Clayey sandstones and siliceous tuffites, or clays overlie the ore-bearing horizon. Total thickness of the Oligocene sediments is 110 m.

The deposit contains primary oxidized (45% of the total reserves), carbonate (40%) and oxidized (15%) ores. The primary oxidized ores can be subdivided into oölitic hard and soft ores composed of pyrolusite, manganite or psilomelane. They contain (w.%) Mn 45-52, Fe 0.7-1.2, P 0.1-1.2, SiO_2 7-12.

The carbonate ores form layers (the thickness is up to 0.5 m) interbedded with sandy-clayey, opal and carbonate-opal rocks. They are composed of manganocalcite, calcite, rhodochrosite and opal. They also contain barite, gypsum, pyrite, and marcasite. The carbonate ores contain (w.%) Mn 10-30 Fe 2-4, P 0.1-0.3, SiO_2 5-40, CaO 10-35.

The oxidized ores, which are the products of hypergene oxidation of carbonate ores, outcropping on the surface, are composed of manganese and iron hydroxides, opal, relics of primary oxidized and carbonate ores. They contain (w.%) Mn 30-35, Fe 2-5, SiO_2 8-35. The highest economic value is attributed to oxidized pyrolusite ores.

IRON-MANGANESE CONCRETIONS (NODULES) OF THE OCEANIC FLOOR

The first iron-manganese nodules on the bottom of the Pacific were discovered by an expedition on "Challenger" vessel 100 years ago. However, real understanding about their development was obtained in the
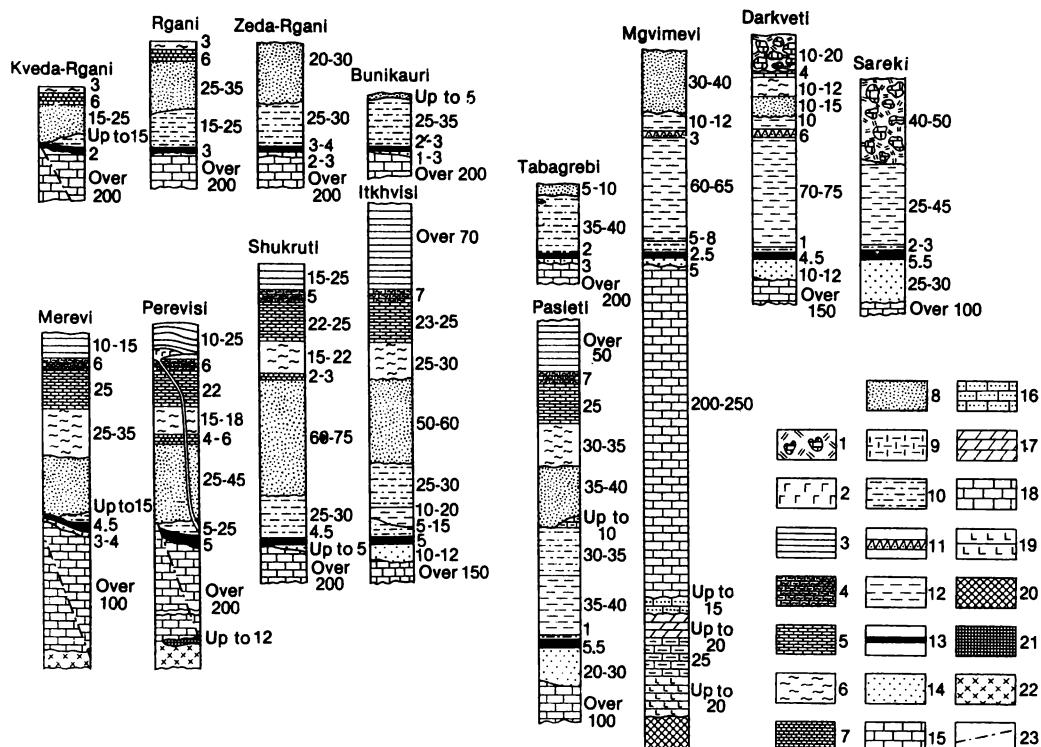
Fig. 18. Lithological columns of the sectors in the Chiatura manganese ore deposit. (After A. Betekhtin, G. Avaliani and V. Tabagari):

1 – caving-diluvial rocks;
2 – basalts;
3 – sandy clays, marls;
4 – clays, marls and oölitic limestones; 5 – oölitic and sandy limestones, coquina;
6 – variegated clays and limestones;
7 – limestones with *Pecten* fossils;
8 – quartz sands and sandstones;
9 – shaly clays;
10 – sandy clays;
11 – upper manganese-bearing horizon;
12 – Maikop facies clays;

13 – the main (lower) manganese-bearing horizon;
14 – sub-ore quartz sands and sandstones;
15 – limestones;
16 – glauconite sandstones and limestones;
17 – marls;
18 – Urgon facies limestones;
19 – sandy limestones and quartz-arkose sandstones;
20 – sandstones and shaly clays;
21 – marl limestones and sandstones;
22 – quartz-porphyries, tuffs and brecciated tuffs;
23 – faults. Rock thickness in metres is given by figures at the right side of each column

second half of this century, when underwater photographing of the oceanic floor was developed together with the methods of recovering deep water sediments. The studies conducted using the above methods established that iron-manganese nodules are mainly forming in the pelagic regions of the ocean and practically are absent in the zones close to continents.

The nodules and ore coatings on the surface of bed rocks are found in pelagic regions practically everywhere both at the bottoms of depressions and on the slopes of uplifts. The thickness of iron-manganese coatings covering basalts and tuff breccias

varies from a few millimetres to 10-15 cm. The size of the nodules may be from 1 mm to 1 m in diameter, most abundant being the nodules with 3-7 cm in diameter.

Morphologic types of such nodules are as follows: spherical, ellipsoidal, lump-like, plate-like, nodular and grape-like (Fig. 19). Such forms are often determined by the configurations of rock fragments or organic residues that serve as nuclei of such nodules. Among the nuclei one can find fragments of effusive and tuffogenic rocks, shark teeth and other organic remnants. The structures of nodules and ore coatings can be as follows: shelly-laminated, oölitic, looped,
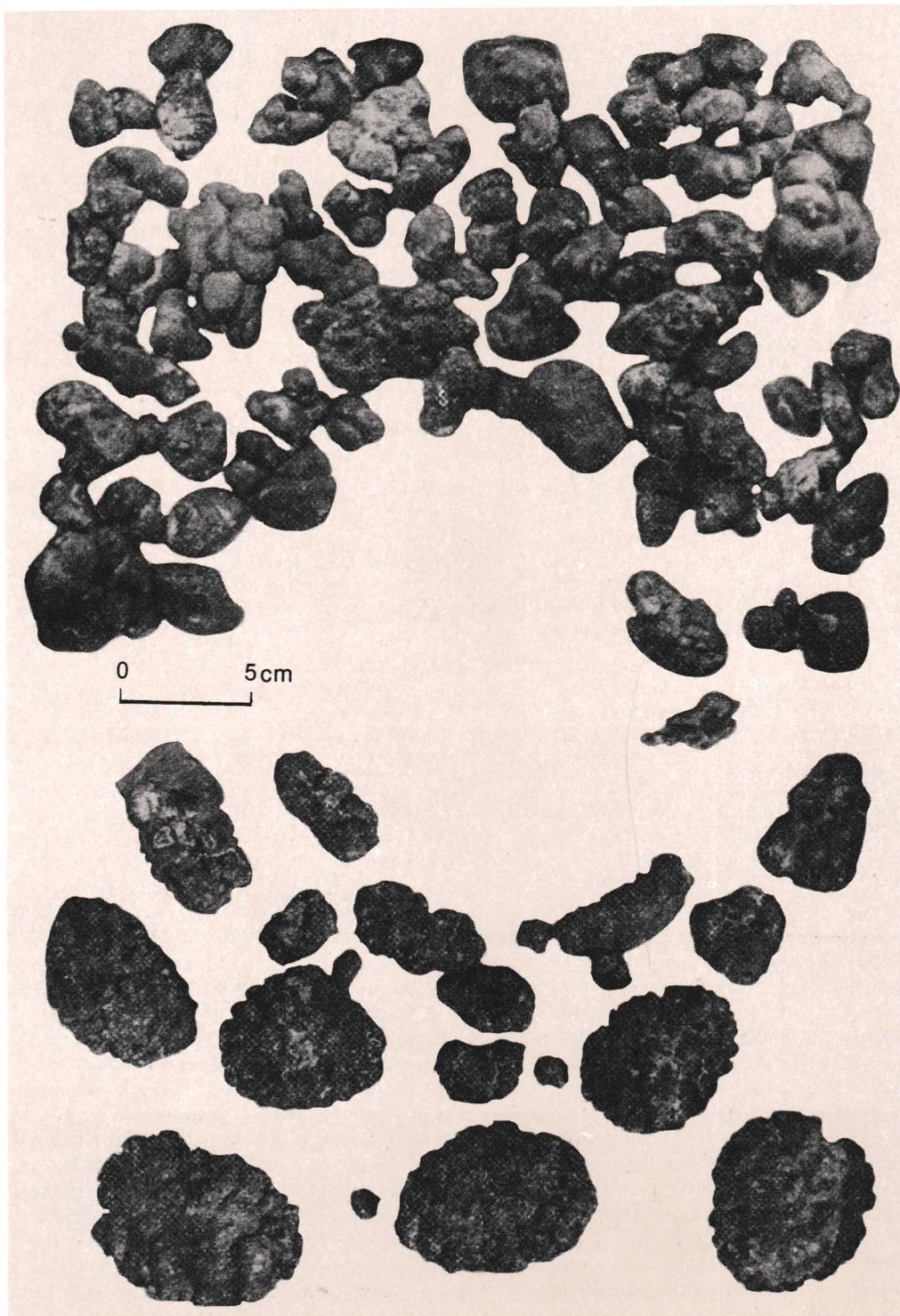
Fig. 19. Selected forms of iron-manganese nodules

colloform, mottled and streaky. They are characterized by different stages of the nodules formation in the process of ore substance precipitation and subsequent processes of metasomatism and meta-morphism. The main ore-forming minerals in nodules are vernadite and hydrogoethite, the other manganese and iron hydroxides (such as todorokite, pyrolusite, birnessite, ranciéite and cryptomelane) are rarely found. Braunite and hematite are identified in composition of metamorphosed nodules (P. Andryushchenko et al, 1976).

The USA, FRG and Japan which do not have large deposits of manganese on their territories have started mining iron-manganese nodules from the Pacific and Atlantic ocean floors from the depth up to 7 km. The nodules mined contain (w.%): Mn 25-30, Fe 10-12, Ni 1-2, Co 0.3-1.5, Cu 1-1.5. Concentrations of such nodules within production areas are 10-20 kg per m^2. The scale of production is 1-2 mln tons a year, which is supposed to expand by 1985 up to 12-15 mln tons a year.

VOLCANOGENIC-SEDIMENTARY DEPOSITS

Volcanogenic-sedimentary manganese deposits compose a large group which is characterized by gradual transitions from the specific sedimentary hydrothermal deposits to subvolcanic ones. They are confined to the areas of an intense underwater volcanic activity which is associated with lava and tuff accumulation, with subordinate amounts of sedimentary rocks and ores. An obvious relation between such deposits and siliceous (jasper, tuffs), carbonate (limestones, dolomites) and fer-ruginous (magnetite-hematite) rocks and ores was established in these areas.

The ores were formed at the early stage of a geosynclinal cycle under eugeosynclinal conditions right after the period of underwater volcanic activity. Inflow of manganese, iron, alumina, copper, zinc, lead, barium and germanium, as well as other components was realized through post-volcanic underwater exhalations and hydro-thermal solutions. Usually, iron-manganese deposits are confined to diabase-porphyry,

or quartz-keratophyre complexes and are located both close to the source of volca-nic activity and at a distance from them among the layers of a pyroclastic material.

The deposits of this group are distinguis-hed by the braunite-hausmannite composi-tion of the primary manganese ores and by the presence of the psilomelane-vernadite ores in weathering crusts. They are repre-sented by sheet-like occurrences of 1-10 m thickness, containing (w.%): Mn 40-55, SiO$_2$ less than 10, P 0.03-0.06. Usually, such deposits are small in terms of their re-serves.

The examples of such deposits in the USSR are the Devonian deposits of the Atasu and Dzhezdy regions in Central Kazakhstan, Mountainous Altai, Magni-togorsk region in the southern Urals, and Cambrian deposits such as Mazulsk and Durnovsk in Kuznetsk Alatau, Uda-Shantar region in Khabarovsk Territory, as well as a number of other small Cretaceous deposits in the Caucasus. (The largest iron-manganese deposit in the Atasu region is the Western Karazhal which has been described in the previous section.)

DEPOSITS OF WEATHERING

Deposits of weathering are formed after manganese-containing metamorphic silicate and carbonate rocks. They mostly occur in India and Brazil, as well as in Canada, Venezuela, Gabon, South African Republic and Australia.

In India commercial value is attached to the deposits of high-grade manganese ores composed of pyrolusite and psilomelane that were formed in weathering crusts (manganese hats) of Proterosoic gondites and kodurites. They contain (w.%) Mn 30-50, SiO$_2$ up to 12, Fe up to 14, P, usually, up to 0.2, sometimes up to 2. The oxidized ores occur down to 10-70 m. A few dozens of large and hundreds of small deposits containing high-grade manganese ores have been found in the Central and Southern states of India (Madhya Pradesh, Maharashtra, Rajasthan, Gujarat, Orissa and Andhra Pradesh).

Manganese deposits in Brazil are associated with ferruginous quartzites,

manganese-containing carbonate rocks and gondites in the states of Minas Gerais, Amapá, Bahia, Goias and Mato Grosso. The deposits in Mato Grosso are of the Cambrian and Ordovician age, while the remaining are Proterozoic.

There are over 50 manganese deposits in the state of Minas Gerais that are related to ferruginous quartzites, and over 100 deposits associated with manganese-containing limestones, dolomites, quartzites and schists that compose the Lower Proterozoic rocks of the Minas series.

The ferruginous quartzites, which have average thickness of up to 150 m, usually contain from 1 to 5 beds or lenses of 0.5-6 m-thickness enriched with manganese. They are traced along the strike over hundreds of metres up to 10 km. They contain 40-50% of manganese, Mn/Fe ratio being 3, while in the gondites this ratio is 8-10 which makes it to distinquish these two ore formations.

Manganese contents in oxidized hypergene ores that were formed after manganese-bearing dolomites are 30-53%. They also contain silica and iron up to 3%, and phosphorus up to 0.1%. These ores differ from the ores formed after silicate rocks by low content of silica and iron.

METAMORPHOGENIC DEPOSITS

Metamorphogenic manganese deposits are related to manganese-bearing Proterozoic silicate rocks, such as gondites and codurites. Gondites are composed of quartz, spessartine, braunite, hausmannite and rhodonite. Codurites are composed of potassic feldspar, spessartine and apatite. They are interbedded with marbles, quartzites and schists. Gondites and codurites are distributed over large areas of hundreds of square kilometres, the length of manganese-bearing deposits ranging from 3 to 8 km, from 3 to 60-m thickness. Average manganese content is 10-20%. The largest such deposits are known in India and Brazil.

In India metamorphosed sedimentary formations of quartzites, schists and carbonate rocks, which include gondites and codurites, as well as metamorphosed manganese ore beds, are known in the

regions of Sausar, Aravalli, Chempener, Gangapur and Kondolit. They occur in the form of belts having up to 200-km length and up to 30-km width. The country rocks are metamorphosed to greenschist and granulite facies. The ore bodies and enclosing rocks are gathered into folds of various sizes. Metamorphosed manganese ore deposits are characterized by banded structure and are composed of braunite, bixbyite and hollandite.

They are interbedded with manganese silicate rocks, gondites and codurites. At present the thickest ore bodies of oxidized manganese ores from the oxidation zone are being mined. Gondites and codurites are not mined.

In the South African Republic in the area of Kuruman (Kalahari) the manganese ore beds are confined to the base of ferruginous quartzites overlain by calcareous dolomites of Upper Precambrian in the Transvaal system. The ore-bearing strata contain three ore beds of 3-m average thickness, with a total thickness of productive beds ranging from 20 to 50 m. The beds are traced along to a few kilometres. The ores are composed of braunite, cryptomelane, rarely, of hausmannite and manganite. Manganese content in the ores is 38-48%, iron is 4-20%.

3 CHROME DEPOSITS

Chromium was discovered by a French chemist N. L. Vauquelin in the crocoite mineral found in the Urals in 1797. Chrome ore (chromite) was first found in the Urals in 1799. Early in the 19th century chromite was only used as refractory material to line the insides of metallurgical furnaces, as well as a paint and tanning agent. By the end of the 19th century chromium started to be broadly used as an alloying metal which improves steel properties.

At present, the main consumer of chromites is metallurgical industry (65%), much less is consumed by refractory industry (18%) and by chemical industry (17%). An addition of ferrochrome (65-70% of Cr, 5-7% of C, the remaining part is of Fe) or charge-chrome (54% of Cr, 6-7% of C, 2-4% of Si, the remaining is Fe) to steels

increases their toughness, hardness and corrosion-resisting (stainless, high-temperature. acid-resisting, tool and other types of steel). The alloys of chromium with cobalt, tungsten or molybdenum are used as corrosion resistant plating (chromium-coating).

The USSR holds the leading place in the world in terms of reserves and production of chromite. Total reserves of chromite in capitalist and developing countries are estimated as 1 670 mln tons. Over 90% of this total is located in South African Republic and Zimbabwe. The remaining 10% is in Turkey, Philippines, India, Iran, Finland and Madagascar. The production of chromite in 1975 was 6.7 mln tons. At present, chromites are produced by 14 countries, the USSR contribution constitutes 40%. The price for chromite, containing 44-48% of Cr_2O_3, is 75-135 US dollars per ton.

Unique deposits of chromite have reserves of hundreds of millions of tons. Large deposits have tens of millions of tons, and small deposits contain a few millions of tons.

Metallurgical industry uses the ores containing more than 48% of Cr_2O_3, provided that the Cr_2O_3/FeO ratio is more than 3 and the content of S and P are less than one per cent. Chemical industry uses the ore containing Cr_2O_3 more than 44%, Fe_2O_3 less than 14%, SiO_2 less than 5%. Refractory industry uses the ore containing Cr_2O_3 more than 32%, SiO_2 less than 6% and CaO less than one per cent.

most abundant in the nature. Hexavalent compounds of chromium are only formed in extremely oxidizing environment at high values of pH. Trivalent chromium, because of its high affinity to oxygen, however, at the time, forms oxide due to similarity of its ions to the ions of aluminum, magnesium, bi- and trivalent iron. It forms complex compounds of these metals, that segregate during differentiation of basalt magma at high temperature magmatic stage of the endogenous process. Under exogenous conditions such compounds also turn to be stable and capable to form placers or migrate in the form of suspensions, thus enriching sometimes sands and clays.

Twenty five minerals containing chromium are known. Commercial value is attributed to chrome-spinellids ("chromite") which have the same chemical formula (Mg, Fe)O·(Cr, Al, Fe)$_2$O$_3$ (Fig. 20). Composition of chromites is variable (w.%): Cr_2O_3 18-65, MgO up to 16, FeO up to 18, Fe_2O_3 up to 30, Al_2O_3 up to 33. They also contain oxides of Ti, Mn, V, Ni, Co, Zn and others. The highest commercial value is attributed to magnochromite (50-65% of Cr_2O_3). Chrome picotite and alumochromite (35-55%) are less important. Other chrome-bearing minerals are chrome vesuvian, chrome diopside, chrome tourmaline, chrome garnet (uvarovite), chrome mica (fuchsite), and chrome chlorite. They are often found in association with chromites or in the zone of hypergenesis (chromates, chrome carbonates and others). These minerals are important as indicators of chrome.

GEOCHEMISTRY AND MINERALOGY

Four isotopes of chromium are known in the nature. They are ^{50}Cr, ^{52}Cr, ^{53}Cr, ^{54}Cr. The most widespread is ^{52}Cr isotope. The clarke of chromium is 0.0083%. Somewhat higher contents of chromium are recorded in ultrabasic (0.2%) and basic (0.02%) rocks. The clarke of concentration of chromium is rather high (around 4000).

Chromium can have two valencies, i.e. Cr^{3+} and Cr^{6+}. Trivalent chromium compounds are the most stable and the

METALLOGENY

In the general course of geological development deposits of chromites were formed twice, i.e. at the early stage of a geosynclinal cycle and at the stage of activization of a platform cycle.

At the early stage of a geosynclinal cycle, the magmatic deposits related to ultrabasites (dunites, and harzburgites) which are the end differentiates of the peridotite formation are formed. Among these deposits the late magmatic formations appear to be the most important. The deep-seated faults that

extend along the borders of eugeosynclinal troughs control the distribution of ore-bearing ultrabasic massifs and chromite deposits related to them which form the extended chromite belts. Chromite-bearing belts in the Urals, Balkan Peninsula and Turkey may be served as an example.

At the stage of platform activization, massifs of stratified rocks of the gabbro-norite formation are developed for which early magmatic chromite deposits are typical.

The majority of geologists consider chrome deposits as the products of magmatic differentiation of basalt melts, that are segregated at the beginning of the process, due to the fractional crystallization of "dry" magmas, or at the end of the process segregating from residual melts enriched with volatiles, which reduce the crystallization temperature of chromites. There are also geologists advocating liquation and metasomatic origin of chromites.

Chromite deposits were formed in different cycles of the geologic development, namely, Proterozoic (India, USA), Caledonian (Norway, South Africa), Hercynian (Urals, Balkan and, probably, most part of Turkey

and Iran), Alpine (Yugoslavia, Albania, Philippines, Cuba, New Caledonia).

TYPES OF COMMERCIAL DEPOSITS

Among the commercial types of chromite deposits one can distinguish (1) early magmatic; (2) late magmatic; (3) placers (insignificant).

EARLY MAGMATIC DEPOSITS

Early magmatic deposits are represented by sheet-like bodies of chromite ores in stratified ultrabasic massifs. The Bushweld massif in the South African Republic and the deposits of Great Dyke in Zimbabwe are the examples of unique deposits by the reserves of this type.

THE BUSHWELD MASSIF (Transvaal province, the South African Republic) is represented by a very large lopolith which stretches from west to east over 460 km and from north to south by 250 km. It gets narrower and subsides toward the centre at 15-30° angle (Fig. 21). The massif intruded
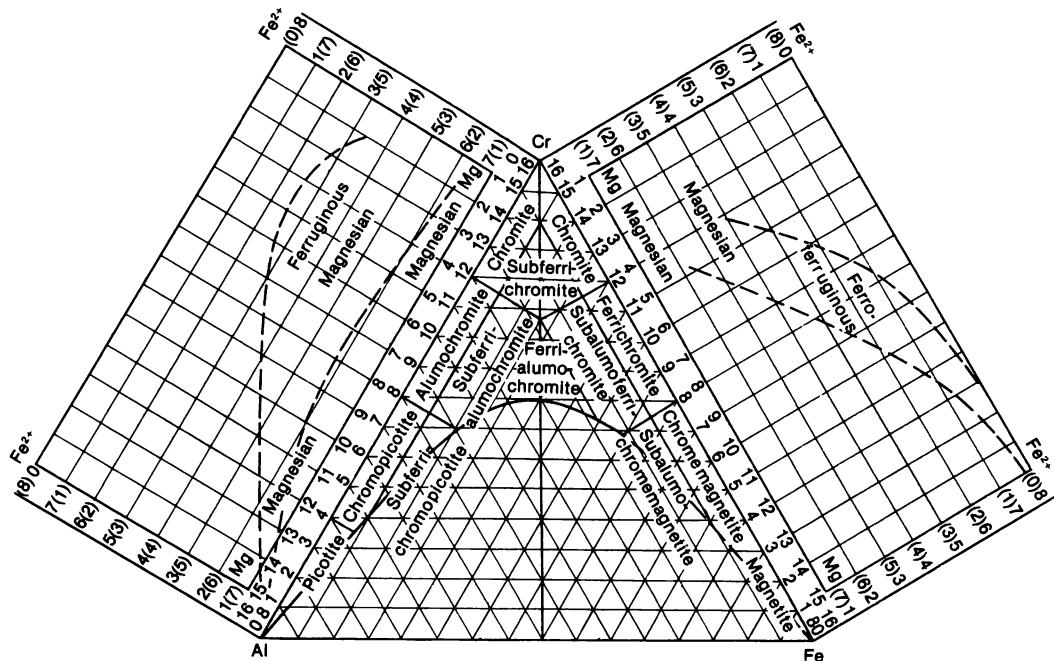

**Fig. 20.** Classification on chrome-spinellides. (After N. Pavlov)
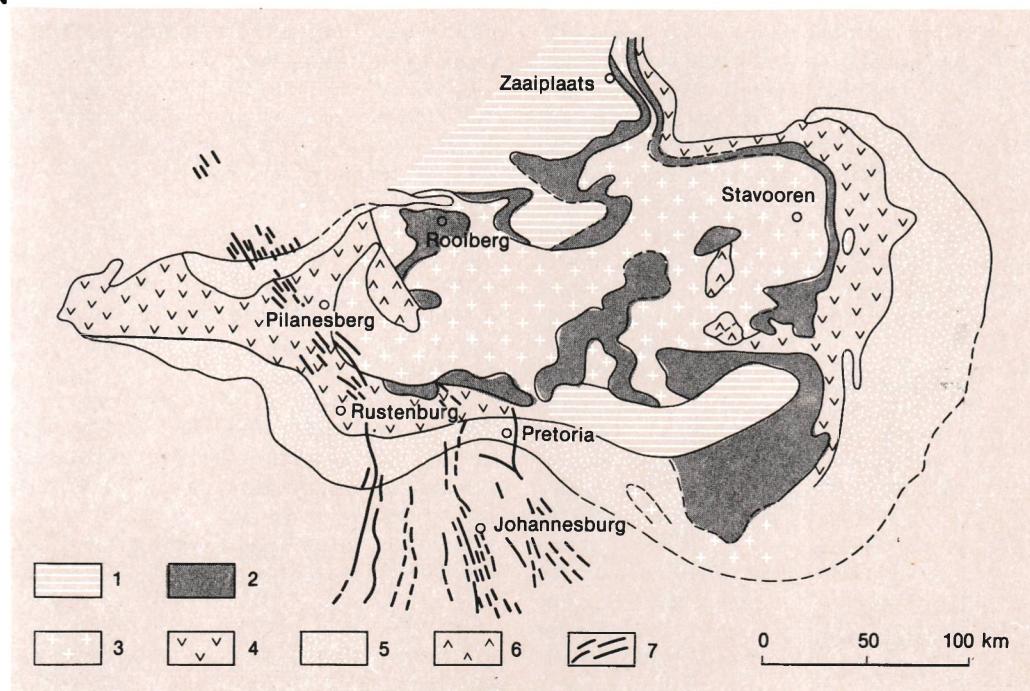
Fig. 21. Geological plan of the Bushveld lopolith. Upper Carboniferous sediments are not shown. (After A. Du Toit):

1 – Lower Paleozoic sandstones and shales;
2 – Lower Paleozoic quartzites and felsites;
3 – granites;
4 – Precambrian norites;

5 – diabases;
6 – syenites and alkaline syenites;
7 – dikes of alkaline rocks

into a very thick strata of Proterozoic quartzites and volcanics (Transvaal system) of the Proterozoic age. The intrusion occurred at the moment of maximum accumulation of sediments and sagging of a large platform trough. The main feature of the internal structure of the massif is its stratification. Individual strata of basic and ultrabasic rocks that have thicknesses varying from a few metres, can be traced strikewise over the distances of up to 100-200 km. The following sequence of rocks from the bottom to top is observed in the massif (Fig. 22): (1) norites having 350-m thickness (the Quenching zone); (2) norites, interbedded with peridotites, of 1 500-m thickness (the Basal zone); (3) norites, with interlayers of pyroxenites and anorthosites, of about 1 000-m thickness (the Critical zone); (4) gabbro-norites of 3 500-m thickness (the Main zone); and (5) gabbro-diorites of 2 000-m thickness (the Upper zone).

The deposits of chromites are concentrated in pyroxenites and anorthosites of the Critical zone. Platinum-bearing copper-nickel sulfide deposits (the Merensky horizon) are related to norites in this zone. The anorthosites of the Main zone contain deposits of titanomagnetites. In the upper part of the massif, granites in association with hydrothermal deposits of tin and fluorite, are known.

The chromite deposits are confined to two ore-bearing horizons extending over 110-160 km. The bodies of disseminated and massive ores have the form of parallel interlayers whose setting is in complete agreement with stratification features of the enclosing rocks. Chromites of nodular texture are also known.

Within the ore-bearing horizons, down to 120 m, up to 25 chromite beds have been revealed, that are combined in three groups. The upper group (down to 30-m depth), the middle group (30-75-m depth) and the lower
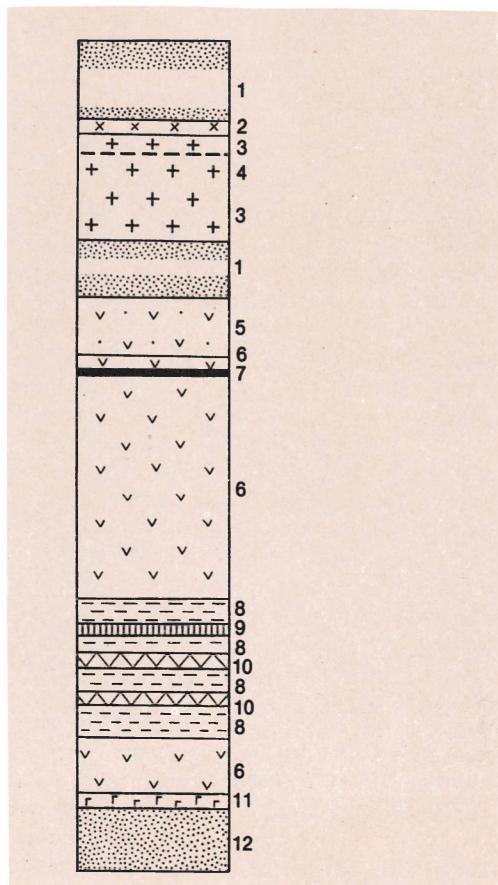
Fig. 22. Diagram of geological column of the Bushveld lopolith. (After A. Du Toit):

1 – quartzites and felsites of the Lower Paleozoic;
2 – granophyres;
3 – granites;
4 – tin and tin-tungsten-copper mineralization;
5 – acid norites, diorites;
6 – norites, anorthosites;
7 – titanomagnetite;
8 – bronzitites, norites, gabbros, anorthosites and dunites;
9 – Merensky horizon;
10 – chromites;
11 – basalts;
12 – Precambrian quartzites

group (down to 120-m depth). The thickness of the beds varies from 0.2 to 1.8 m. Chromites of the lower group of the beds contain 42-50% of Cr_2O_3. The ratio of Cr_2O_3/FeO in these beds varies from 1.8 to 2. The chromites of the middle and upper groups contain 32-46% of Cr_2O_3 with Cr_2O_3/FeO ratio 1.5-1.75. The reserves of chromite in this deposit are estimated as 500

million tons with average content of chromium oxide being 45%.

THE GREAT DIKE intersects the central part of Zimbabwe striking from south to north along 17° and having almost the vertical dip. The length of the dike is 560 km and the width is 3-13 km. The dike is composed (from floor to roof) by serpentinized dunites, harzburgites, pyroxenites, gabbro and norites. Sheet-like deposits of chromites are located at the bottom part of the intrusive among dunites and harzburgites. The deposit contains up to 11 ore interlayers of 16-72-cm thickness located one above the other at an average distance of 6 m. They are traced over a few kilometres. The ores are of high grade and contain 48-50% of Cr_2O_3 and up to 11% of Fe_2O_3. The total reserves of chromite are estimated to be 300-500 million tons.

LATE MAGMATIC DEPOSITS

Late magmatic deposits are well known in the USSR in the Urals, Caucasus, in Siberia, Chukotka, Kamchatka, Sakhalin and also in other countries, such as Albania, Greece, Yugoslavia, Turkey, Iran, Pakistan, India, Philippines, Madagascar and Cuba.

The Urals is the main chromite province of the USSR. Altogether 25 regions, which produced chromites at different times, are known in this region. At present, the Don group of chromite deposits, located in the South-Eastern part of the Kempirsai massif in the Southern Urals, and the Saranovsk deposit situated in the western slope of the middle Urals are being mined.

THE KEMPIRSAI MASSIF. This massif of ultrabasic rocks is located within the Uraltau meganticlinorium. It extends in submeridional direction over 82 km in conformity with a controlling fault zone. The width of the massif varies from a few kilometres in the north to 32 km in the south.

The northern part of the massif is conformable with the foliation of Upper Proterozoic sediments in the hanging wall, and with that of Ordovician sediments in the footwall. This part of the massif is represented by a monoclinal westward dipping body with a thickness of up to 2.5 km and with the dip angle from 40 to 60°. On the surface of the massif there are
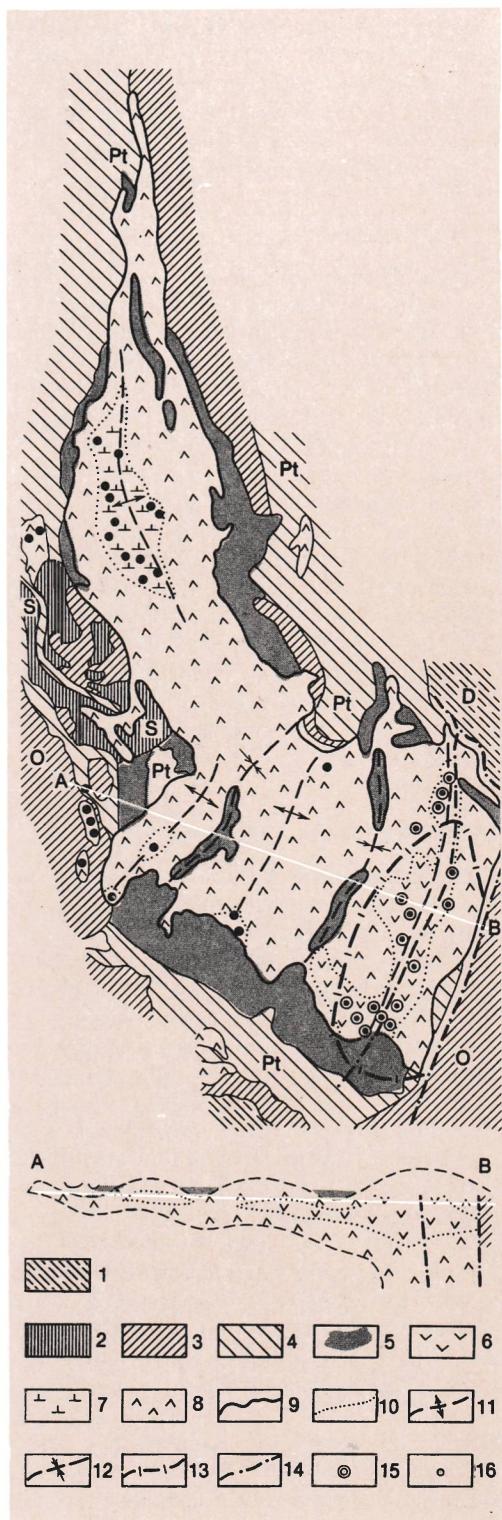
three dome uplifts. Xenoliths of the roof composed of gabbro-amphibolites and Upper Proterozoic schists were observed in the depressions between the uplifts. According to geological and geophysical data, the massif in its southern part has the shape of a laccolith (Fig. 23), which lies between the Upper Proterozoic and Lower Paleozoic rocks. Below the south-eastern and northern chromite-bearing parts of the massif, geophysical surveys revealed a feeding channel having steep east dipping toward the Magnitogorsk synclinorium. The age of formation of this intrusive is 400-380 mln years (N. Pavlov et al, 1968).

The massif is composed of peridotites (harzburgites) and dunites subjected to various degrees of serpentinization. Within the massif over 160 chromite deposits and occurrences are known. They are located in four ore fields: West Kempirsai, Stepnoye (South-West), Tygashai (Central) and Main (South-Kempirsai).

All commercial chromite deposits (Almaz-Zhemchuzhina, after 40 years of KazSSR, Molodyozhnyi, Millionnyi, after 20 years of KazSSR, Komsomolskii, Spornyi, Gigant, Geofizicheskii and others) are located in the South-Kempirsai ore field. The deposits are confined to two submeridional zones, i.e. Western and Eastern (see Fig. 23), each having the length of 20 km. Serpentinized dunites are the enclosing rocks of large chromite deposits. Dunites, in close vicinity to the ore bodies, contain schlierens of disseminated chromite ore

Fig. 23. Geological structure of the chromite-bearing Kempirsai massif. (After N. Pavlov and I. Grigorieva):

1-4—siliceous and carbonate country rocks:
1—Devonian;
2—Silurian;
3—Ordovician;
4—Proterozoic;
5—gabbro-amphibolites;
6—serpentinized peridotites and dunites;
7—serpentinized dunite-peridotite schlieren-banded complex;
8—serpentinized peridotites;
9—contour of the ultrabasic massif;
10—boundaries of ultrabasic rock complexes;
11—axes of the vault uplifts;
12—axes of the intervault subsidences;
13—projection contour of the supplying channel;
14—faults;
15—chromium-rich deposits;
16—deposits of low grade chromium ores;

(0.5-1 m crosswise), thin (1-10 cm) veins and streaks of massive chromite, as well as sulfide-containing (pyrrhotite, pentlandite) dunites.

The contacts between chromites and enclosing ultrabasic rocks are usually clear-cut, normal, occasionally tectonic. The ore bodies wedge out updip and downdip bluntly, very seldom they split. The most widespread shapes of the ore bodies are linear-stretched vein-like lenses, occasionally isometric lenses and pillar-like bodies. Dipping angles of the ore bodies are 5-15°, rarely they may be up to 45°. Depth of occurrence varies from subsurface to 1 200 m. There is no drilling information about deeper horizons.

The size of individual ore bodies varies within broad limits, from a few tens of metres to 1.5 km strikewise, with thickness varying from a few metres to 150 m. The number of ore bodies which constitute deposits may also be variable. The Molodyozhnyi deposit, for example, is represented by one large ore body. Whereas the Almaz-Zhemchuzhina deposit contains five bodies, the deposit named after 40 years of KazSSR has 15 bodies and the Millionnyi deposit has 99 bodies. All deposits have their ore bodies mainly cut into separate blocks by sublatitudinal thrusts-faults. Sometimes, the blocks are displaced by over a few tens of metres to 300 m.

The ores have massive, disseminated and nodular structures and are composed of magnochromite, and, in subordinate quantities, by alumochromite, olivine or serpentine which develops after olivine. The ores also contain chrome diopside, chrome actinolite, chlorites, rutile, uvarovite, tremolite, talc, sulfides (pyrrhotite, pentlandite, chalcopyrite, pyrite, millerite), and brucite, quartz, and exogenic minerals (such as chalcedony, hematite, nontronite, magnesite, anhydrite and dolomite).

The average content of minerals in the ores (w. %) is: chrome spinellides from 80 to 90, serpentine from 5 to 15, carbonates from 4 to 7, other minerals are represented in the quantities less than 1%. In terms of chemical composition, the South-Kempirsai deposits are classified as high-grade ores with low content of ferrous oxide, silica, calcium oxide, sulphur and phosphorus. The massive chromites contain 55-63% of Cr_2O_3, densely disseminated ores contain 44-55% of Cr_2O_3. Alumina content in such ores is 8-15%, magnesium oxide is 10-30%. The Cr_2O_3/FeO ratio is more than 4.

PLACER DEPOSITS

Elluvial-diluvial placers of chromites form as a result of weathering of parent magmatic deposits. They are represented by boulder ores of the Saranovsky deposit, elluvial placers of the Alapayevskii and Warsaw deposits in the Urals, powder ores of weathering crusts in the upper levels of the deposits in the South-Kempirsai region. Similar deposits are also known in Cuba, Philippines, New Caledonia and in the deposits of the Great Dyke in Zimbabwe.

Coastal marine placers are known in the Pacific coast in the state of Oregon in the USA, and on the Terpeniya Bay coast on Sakhalin Island in the USSR. They are also found in the coastal areas of Adriatic Sea in Albania and the Mediterranian Sea in Turkey.

4 TITANIUM DEPOSITS

Titanium, which was discovered in 1791 by the English chemist W. Gregor, found a broad application as a metal of unique properties only in the middle of the 20th century. Its melting point (1 725 °C) is higher than that for iron and nickel, whereas its density is almost twice as less. Titanium has very high strength and corrosion resistance.

Titanium alloys are applied as construction metal in aircraft industry and shipbuilding, in power machine construction, hydrolysis, food and medical industries, and nonferrous metallurgy as well. Titanium alloys have been reliably and efficiently exploited in many chemical aggressive media within the range of temperatures from cryogenic temperatures up to + 500-600 °C and higher. Titanium-vanadium alloys are most important which have high strength, malleability and weldability. Titanium carbide is used to manufacture superstrength alloys, while titanium dioxide is applied to manufacture durable titanium

white pigments, plastics and in pulp and paper industry.

Total reserves of titanium dioxide in capitalist and developing countries are estimated to be 230 mln tons. 90% of the reserves is located in Canada, Norway, USA, India, Egypt and Australia. Production of titanium concentrates in 1975 was 3.4 mln tons (including 90% of ilmenite and 10% of rutile concentrates).

Main producers of titanium concentrate are Australia, USA and Norway. Australia, India and Japan produce synthetic rutile from ilmenite. Production of metallic titanium is underway in the USSR, USA, United Kingdom and Japan. The price for ilmenite concentrate in 1975 was 55 US dollars per ton, and that for rutile concentrate 190 US dollars per ton.

Unique primary deposits of titanium have reserves of tens of millions of tons. Large deposits have a few millions of tons, small deposits have reserves of hundreds of thousands of tons of titanium dioxide. The figures for placer deposits are halved.

Commercial deposits are those that contain over 10% of TiO_2 in the ores in primary deposits, and over 10% of ilmenite, or 1.5% of rutile in placer deposits. Undesirable admixtures are Cr, P and S.

GEOCHEMISTRY
AND MINERALOGY

Five isotopes of titanium are known: ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti and ^{50}Ti. The most abundant is ^{48}Ti. The crustal abundance (clarke) of titanium is 0.45%. Heightened concentrations of titanium are known in basic (0.9%) and intermediate (0.8%) intrusive rocks. The clarke of concentration of titanium is low, i.e. about 20.

Under natural conditions titanium is tetravalent. It occurs only in oxygen compounds. Heightened concentrations of titanium are typical for gabbro, hornblendites, pyroxemites and alkaline rocks of the agpaitic series. Titanium minerals are resistant to weathering and form considerable concentrations in placers.

At present, over 70 titanium minerals are known. Many minerals contain titanium as an admixture. Commercial production of

titanium is mainly based on ilmenite ($FeTiO_3$ 31.6%) and rutile (TiO_2 60%). Ilmenite and rutile also contain vanadium, scandium, tantal and niobium. Extraction of ilmenite from titanomagnetite is only possible if grains of ilmenite exceed 0.3 mm in size. Partially, titanium is extracted from leucoxene, which is the final product of ilmenite and sphene alterations (ilmenite leucoxene contains 96% of TiO_2 and sphene leucoxene contains 67% of TiO_2). Also, titanium can be extracted from anatase (polymorphic modification of TiO_2) and loparite (Na, Ce) TiO_3 (26.6% of Ti).

According to N. Belov, TiO_2 occurs in the form of rutile, if a mineral-forming medium contains iron. If iron is not present, anatase is formed.

METALLOGENY

The deposits of titanium were mainly formed at the early stage of a geosynclinal cycle in connection with well differentiated intrusions of gabbro-pyroxenite-dunite formation. Among them, I. Malyshev distinguishes two main groups: (1) the deposits in anorthosites with ilmenite and rutile-ilmenite ores; (2) the deposits in gabbro with ilmenite-magnetite ores. A transition from ilmenite ores to magnetite-ilmenite ores is related to increasing degree of oxidation during crystallization of a magmatic melt.

Formation of multiphase plutones of alkali and ultrabasic composition with loparite, perovskite and titanomagnetite mineralization is related to zones of reactivation within ancient platforms. As a result of decomposition of rocks containing ilmenite, rutile and anatase, the coastal-marine, proluvial and alluvial placers were formed, among which both the ancient (fossil) deposits of Paleozoic, Mesozoic and Tertiary age and recent formations are known.

Titanium deposits belong to the products of different epochs, such as Precambrian (Baltic shield, Canadian shield, India, South Africa and others), Caledonian (South Africa, Norway, Urals), Hercynian (Urals), and Alpine (North and South America).

TYPES OF COMMERCIAL DEPOSITS

Among commercial deposits of titanium one can distinguish (1) magmatic; (2) placers; (3) weathering; (4) sedimentary-volcanogenic; and (5) metamorphogenic.

MAGMATIC DEPOSITS

The most important commercial magmatic deposits of titanium are confined to large massifs of anorthosite formation having the area of hundreds and thousands of square kilometres. In the Soviet Union such deposits are represented in Eastern Sayan (Maly-Tagul, Lysanska, Kruchinino) and by those of Chineiskii massif (Chita province, on the route of Baikal-Amur Railroad), and by the La Tuque deposit in Canada, as well as by others.

THE MALY-TAGUL DEPOSIT. This deposit contains ilmenite-titanomagnetite ores and is located in the Irkutsk province. It is confined to a massive of gabbro-anorthosites of the same name having the area of over 200 km^2. The deposit has six ore fields which contain ore bodies with commercial content of iron and titanium. In plane, the ore bodies have the dimensions from 50 × × 100 up to 130 × 850 m. Their dipping is steep and is traceable down to 300 m. Iron content in the ores is 20-33%, the content of TiO_2 in the magnetite concentrates is 12-16%.

THE LA TUQUE DEPOSIT. It is the largest deposit of hematite-ilmenite ores in the world located in the Quebec region and possessing 125 mln tons of the ore. The deposit produces around 80% of ilmenite concentrate in Canada, containing 35% of titanium dioxide and 40% of iron. The deposit lays in an anorthosite massif of oval shape with the dimensions of 150 × 50 km. It contains three ore bodies of sheet-like shape that gently steep in conformity with the structure of the massif. The main ore body has the area of 1 km^2 and 90-m thickness. The ore bodies contain numerous inclusions of anorthosite xenolith. High-grade ores are composed of ilmenite (75%) and hematite (20%). Associated minerals are represented by sulfides (pyrite, chalcopyrite,

pyrrhotite), feldspars, pyroxenes and sometimes biotite. The content of TiO_2 in high-grade ores varies from 32 to 36%, the content of Fe is 39-43%. The deposit is considered as a late magmatic formation related to the processes of accumulation of the residual ore melt and its intrusion into tectonically weakened zones of anorthosite rocks (fissure intrusions).

In the USA, 50% of ilmenite production comes from the deposits of a similar type called Tegavus which have reserves of 100 million tons, with TiO_2 contents of 9-12%.

PLACER DEPOSITS

Among placer deposits of titanium two varieties can be distinguished, i.e. coastal-marine and continental.

Coastal-marine complex ilmenite-rutile-zircon placers represent main deposits of this type. Lower importance is attributed to continental alluvial-diluvial placers of ilmenite. The contemporary coastal-marine placers are mined for rutile and ilmenite in Western Australia, India, Sri Lanka, Sierra Leone and, partially, in Brazil and USA. Large reserves of ilmenite sands have been revealed on the northern coast of Greenland, eastern coast of Madagascar, along the coasts of the Malawi Lake, and on the coasts of Mozambique and New Zealand.

In the USSR the main importance is attributed to the old coastal-marine placers in Neogene sediments and Paleogene of Stavropol uplift, and in Paleogene sediment of Ural region, North Ustyurt, Turgay depression, south-western part of the West Siberian plate, in Paleogene and Mesozoic sediments of Chulym-Yenisei and Amur-Zeya depressions, in Mesozoic depressions of the Urals fold system, Pre-Yenisei part of the West Siberian plate, Irkutsk coal basin, and in Paleozoic sediments of Timan and Tom'-Kolyvan' uplifts.

The coastal-marine ilmenite-rutile-zircon complex placers typically have large dimensions and reserves. They form sheet-like or lenticular beds with the thickness of tens of metres and the length of a few tens of kilometres. The width of such
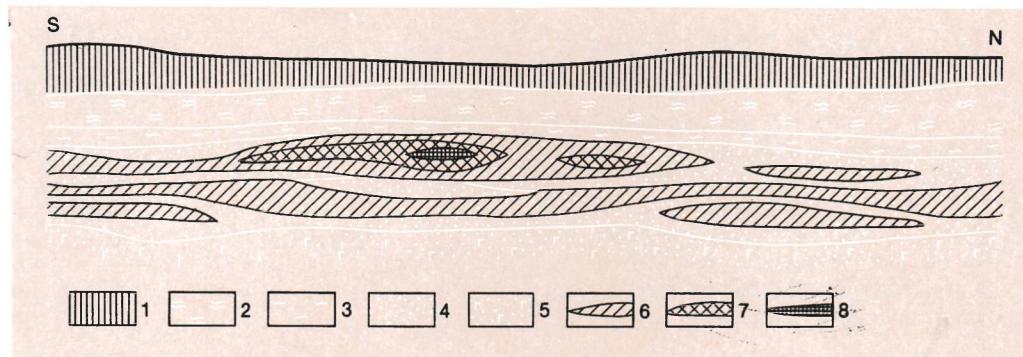
Fig. 24. Cross section of the Sarmatian ilmenite placer in the Pravoberezhnyi region. (After M. Veklich et al):

1 – loess and loess-like loams;
2 – clays and loams;
3 – clays;
4 – quartz sands;
5 – quartz-glauconite sands;

6-8 – heavy minerals content;
6 – low;
7 – high;
8 – very high

deposits may reach one km. In terms of composition, the coastal-marine placers are usually of oligomictic nature. The ore-forming mineral of such placers is quartz; kaolinite has less importance. The sands in the deposits are usually fine and very fine grained. Commercial content of ilmenite and rutile in such placers varies from tens to hundreds of kilograms per cubic meter. Continental weathering crusts developed over coastal-marine placers – crystalline rocks, extrusive sheets, massifs of granite and other rock in massifs.

Continental placers of ilmenite occur mainly in alluvial, eluvial and proluvial Quaternary, Paleogene and Lower Cretaceous sediments. The ore bodies of alluvial placers typically have band-like shapes confined to river valleys. Ore minerals were accumulated at lower levels in the most coarse fragmental material represented by coarse-grained sand, pebble or small-size gravel. In terms of mineral composition the continental placers are usually polymictic (quartz, feldspar, kaolinite). Ilmenite grain size can be 0.1-0.25 mm and more. They are slightly rounded. Ilmenite content in commercial continental placers varies from a few tens to several hundreds of kologrammes per m³.

Below the Pravoberezhnyi deposit of the Dnieper region is described as an example

of a coastal-marine placer and the Irsha deposit of the Volodarsk-Volynsk district is described as a continental placer.

THE PRAVOBEREZHNYI DEPOSIT. The coastal-marine placers of this deposit are confined to Poltava and Sarmat sandy-clayey sediments of 10-60-m thickness overlain by loess, loess loams and clays of the Neogene and Quaternary age. The ore beds have sheet-like shape with a very pronounced domination of length over width, and show a considerable thickness of productive sands. Clearly horizontal or gently steeping (2-10°) bedding of the ore-bearing sands is emphasized by an accumulation of mainly titanium and zirconium heavy minerals (up to 70-90%). The ore minerals in the Poltava sands occur in the upper part, whereas in the Sarmatian sands they are distributed throughout the whole profile.

The ore-bearing sands of both ages have similar mineral composition, namely, leucoxenized ilmenite (44%), rutile (16%), zircon, disthen, sillimanite, staurolite, tourmaline (about 10% each). Chromite, anatase, brookite, corundum, xenotime and other minerals are found in small quantities. Minerals, as a rule, are fine grained (0.1-0.2 mm) and well rounded. Productive deposits of the Sarmatian age occur on top of the Poltavian series sands enriched in heavy minerals (Fig. 24). They were formed

at the expense of redeposition of Poltavian sands in the coastal-beach zone of the Middle Sarmatian Sea.

THE IRSHA DEPOSIT. It was formed during rewashing of the kaolinite weathering crusts in the Volodarsk-Volynsk gabbro-anorthosite massif. The Quaternary placers usually occur in submorainial sands within the interfluves and terraces of the Irsha river. Their thickness is 1-15 m, and the ilmenite content varies from tens to 100-200 kg/m³.

DEPOSITS OF WEATHERING

Modern and buried titanium-bearing weathering crusts are formed over gabbro-anorthosites (Volyn' massif) and metamorphic rocks (the Ukrainian shield, Kazakhstan). In the course of leaching of alkaline elements, and formation of clay minerals, belonging to the kaolinite group, the crusts tend to accumulate more stable accessory minerals, including ilmenite and rutile. In this case the grains of ore minerals maintain their initial shapes of crustals and do not yield to rounding. The thickness of weathering crusts may reach a few tens of metres. Ilmenite content may reach a few hundreds of kilograms per cubic meter, that for rutile may be a few tens of kilograms per cubic meter.

The mineral composition of parent rocks substantially influences the qualitative and quantitative contents of ore minerals in weathering crusts. For example, for the Volyn' gabbro-anorthosite massif, the crusts enriched only in ilmenite (300-500 kg per m³) are characteristic which is due to the absence of rutile in parent rocks (I. Malyshev, 1957). The weathering crusts of the Kundybay deposit in Kazakhstan were formed over metamorphic rocks, they contain up to 180 kg/m³ of ilmenite and up to 74 kg/m³ of rutile.

SEDIMENTARY-VOLCANOGENIC DEPOSITS

THE NIZHNY MAMON. The deposit is confined to the titanium-bearing volcanogenic-sedimentary formations in the south of the Voronezh region near the Nizhny Mamon village. The deposit is composed of sedimentary and volcanogenic-sedimentary Paleozoic, Mesozoic and Cenozoic rocks, concordantly occurring on a Precambrian basement. The deposits of Yastrebov horizon of the Devonian age have the thickness ranging from a few metres to 35 m. The depth of occurrence of the horizon is 50-70 m. Total lenght of the area covered by volcanogenic-sedimentary rocks is approximately 100 km, with the width of 20-40 km.

The main striking direction coincides with the fault zone to which a volcanic activity in the area is related. The highest content of ilmenite is found in coarse fragmental tuffs, tuffites and tuff-sandstones, where effusive fragments are typically represented by the rocks of basic composition. Terrigenous material in tuffs is less or equal to 10%, while that in tuff-sandstones is less or equal to 90%. Magnesial-ferruginous chlorite acts as a cement in this terrigenous material. Coarse fragmental varieties of tuffogenic rocks are the most enriched in ilmenite (sometimes its content reaches 50% of the volume). The ilmenite grain size, in average, is 0.25-0.3 mm. Ilmenite content drops sharply with an increase of the content of the terrigenous material. Formation of volcanogenic rocks, enriched in ilmenite, probably took place in a shallow marine basin and was a result of underwater volcanic activity.

METAMORPHOGENIC DEPOSITS

The titanium deposits of metamorphosed and metamorphic groups are incorporated into this series.

Metamorphosed Deposits

Metamorphosed titanium deposits were formed during metamorphism of ancient placers and primary magmatic ores. The Upper Proterozoic metamorphosed placers within the Bashkir uplift are confined to sandstones of the Zilmerdak suite with ilmenite and zircon rich interlayers having the thickness of up to 2.5 m and containing up to 250-400 kg per ton of ilmenite and up to 30 kg per ton of zircon.

High-grade massive ilmenite-magnetite and disseminated ilmenite ores are formed during regional metamorphism of primary magmatic ores as well. The Otanmäki deposit in Finland is an example of commercial deposits of such type, confined amphibolites formed as a result of metamorphism of ore-bearing gabbro. High-grade ores of this deposit contain, in average. 12% of TiO_2.

THE YAREGA DEPOSIT. An unusual representative of this group is the Yarega deposit of leucoxene (Southern Timan) which is confined to oil-bearing sandstones of the Eifelian and Givetian stages. The deposit is represented by a buried metamorphosed Devonian placer. Productive beds occur on Riphean metamorphic schists. The lower ore horizon is composed of coarse-grained quartz sandstones with interlayers of aleurolites and argillites. The upper horizon is composed of polymictic conglomerates and inequigranular quartz sandstones. Ore minerals are represented by semi-rounded grains of leucoxene of 1-1.5-mm size and by rare grains of ilmenite. The samples of high-grade ore taken from the sandstone contain 8-10% of TiO_2.

The deposit was formed, probably, as a result of erosion of the weathering crusts developed over the Riphean metamorphic schists.

Metamorphic Deposits

Titanium metamorphic deposits are confined to ancient crystalline schists, gneisses, eclogites and amphibolites. Such deposits are formed as a result of metamorphism of intrusive, volcanic and sedimentary rocks enriched in titanium. Precambrian chlorite schists containing up to 20% of rutile (the deposit of Harvard, USA) and Precambrian gneiss containing up to 25% of rutile (the Pluma Hidalgo deposit in Mexico) are the examples of this type of deposits.

The Kuznechikha deposit (the Middle Urals) contains around 1.5% of rutile in amphibolites. Eclogites of the Shubinsk deposit (the Southern Urals) contain 4.5% of rutile.

5 VANADIUM DEPOSITS

Vanadium was discovered in 1801 by a Mexican mineralogist Del Rio. For the first time this element began to be used early in the 20th century when it found its application for alloying steel and iron. This metal also facilitates a removal of oxygen and nitrogen from iron and steel, thus producing a dense casting with fine grains and thin walls. Vanadium improves hardness, elasticity and rupture strength of the alloys, facilitates the decrease of structures weight, and raises wear resistance and weldability of steel.

Iron alloyed by 35-80% of vanadium produces ferrovanadium and its substitutes (carvan, solvan, ferrovan and nitrovan) that are used in ferrous metallurgy for alloying (90% of all vanadium produced). Titanium-vanadium alloys (vanadium content up to 17%) are used to manufacture parts of jet aircrafts and space engineering. Vanadium alloys with Ca, Ta, Nb, Zr, Ni, Co, Al, and Mg are also broadly used. Cast iron alloyed with 0.1-0.35% V is broadly used in machine building to manufacture those parts of mechanisms that work under heavy loads. Steels alloyed by vanadium (up to 1-5%) are applied to manufacture high-speed cutting tools (together with Cr, W and Mo).

In chemical industry vanadium is used as a catalyst in oil cracking, in production of acids, aniline dye production, and rubbers, as well as a painting ingredient added to glass or ceramic. Vanadium is also used to manufacture colour films.

Total reserves of vanadium pentaoxide in capitalist and developing countries are estimated to be 6.7 mln tons, 85% of the total is located in South African Republic and Australia. The remaining reserves are distributed in India, USA, Finland, Norway and Namibia. Vanadium products (thousands of tons of V_2O_5) are produced in South African Republic – 19, USA – 7.5, Finland – 2.3, Norway – 2, Namibia – 1. The price for commercial vanadium pentaoxide in 1975 was 5-7 US dollars per kg. Ferrovanadium and its substitutes were sold in that year at the price of 12-14 US dollars per kg of vanadium.

The majority of deposits having the ores

from which vanadium is extracted are of a complex composition. Vanadium is produced as a by-product with the main components of the ores, such as Fe, Ti, U, Pb, Zn, P, and in some cases with oil. In the USSR the main raw material for vanadium production are titanium-magnetite ores. After blast furnace melting of these ores almost all vanadium is transferred into pig iron. After conversion of pig iron into steel, the remaining slag contains up to 25% of V_2O_5. The slag is roasted with sylvinite or soda and is then subjected to leaching which produces commercial vanadium pentaoxide. When it is molten with iron, ferrovanadium is produced.

Capitalist and developing countries produce about 70% of vanadium from titanomagnetite and ilmenite-magnetite ores. The remaining part is produced from uranium-vanadium, carnotite, roscoelite ores, phosphorites, clays of argillitization zone, oxidized polymetallic ores, oil and bauxites.

Unique deposits of vanadium are those which contain millions of tons of V_2O_5; large-size deposits contain hundreds-tens of thousands of tons. Small deposits contain a few thousands of tons of V_2O_5. The minimum content of vanadium pentaoxide in a titanomagnetite concentrate is 0.3%. Undesirable admixtures are CaO and P.

GEOCHEMISTRY
AND MINERALOGY

Two stable isotopes of vanadium are known in the nature. One of them ^{50}V is rare and another ^{51}V is widespread. The crustal abundance (clarke) of vanadium is 0.009%. Heightened contents of vanadium (0.02%) are known in gabbro and basalts. The clarke of vanadium concentration is 30.

Only trivalent vanadium compounds are known in magmatic formations. Vanadium in hypogenic processes occurs in a dispersed state because the radius of V^{3+} ions is very close to those of Fe^{3+} and Ti^{4+} that are abundant in magmatic rocks. Vanadium is concentrated in the minerals which contain iron and titanium, such as titanomagnetite, sphene, rutile, ilmenite, pyroxenes, amphiboles and garnets (L. Borisenko, 1973).

Hydrothermal formations contain minerals of tri- tetra-, and pentavalent vanadium. The tendency of vanadium to form complex compounds with halogens (Cl, F) assists in its transportation by hydrothermal solutions.

Under exogenous conditions vanadium is transported by river and sea waters in the form of suspensions and true solutions (VCl_3, VCl_4, $VOCl$, $VOCl_3$), it is also adsorbed by hydrooxides of iron, aluminium and organic substances. In the zone of hypergenesis the solutions enriched in vanadium easily form vanadates, i.e. salts of orthovanadic acid (H_3VO_4).

About 70 minerals are known that contain vanadium. Over half of them are represented by vanadates, the remaining part is classified as oxides, silicates and sulphides. Besides, there are numerous vanadium-containing minerals, with vanadium content in the range of 2-10%.

Commercial minerals of vanadium are as follows: titanomagnetite (with V_2O_5 content 0.3-10%), roscoelite $KV_2AlSi_3O_{10}[OH]_2$ (19-29%), carnotite $K_2U_2[VO_4]_2O_4 \cdot 3H_2O$ (20%), vanadinite $Pb_5[VO_4]_3Cl$ (19%), descloizite (Zn, Cu)$Pb[VO_4]OH$ (20-23%), and patronite VS_4 (29%).

METALLOGENY

Under endogenous conditions vanadium enters the composition of titanomagnetite and ilmenite-magnetite magmatic deposits that were formed at the early stage of a geosynclinal cycle in connection with intrusions of a gabbro-pyroxenite formation. Under exogenous conditions vanadium is associated with sedimentary strata of carbonaceous-siliceous black shales of a geosynclinal cycle, as well as with sedimentary ores of iron, bauxites and coals of a platform stage and the zones of oxidation in uranium-vanadium and polymetallic deposits. The main endogenous deposits of vanadium are located among the formations of Proterozoic and Caledonian metallogenic epochs. For exogenous deposits V. Kholodov (1968) distinguishes eight epochs of formation, the most important ones among them are the global Lower Paleozoic epoch when metal-bearing carbonaceous-siliceous shales were most

widespread, and the Meso-Cenozoic epoch of formation of marine and fluvial oölitic iron ores that appear to be the concentrators of vanadium.

TYPES OF COMMERCIAL DEPOSITS

Commercial deposits of vanadium are as follows: (1) magmatic; (2) weathering; (3) placers; (4) sedimentary; (5) metamorphogenic.

MAGMATIC DEPOSITS

The largest massifs of vanadium-bearing ultrabasic and basic rocks with the areas reaching several hundreds and even thousands of square kilometres, are related to the anorthosite formation, (Canadian shield) and the formation of differentiated gabbro and norite intrusions (Bushveld complex). A few tens of square kilometres is the area of the gabbro-pyroxenite-dunite formation to which the deposits of vanadium-containing titanomagnetites in the Urals are related. The reserves of vanadium in individual deposits of the above formation may reach a few millions of tons with average vanadium contents in the ores ranging from 0.1 to 1%. The main minerals that concentrate vanadium are titano-magnetite and magnetite. In most cases these minerals crystallized after silicates, the fact which is being supported by sideronitic structure of the ore. The highest contents of vanadium are observed in the ore minerals of basic rocks, lower contents are recorded in the rocks of ultrabasic composition.

The Kachkanar iron ore deposit in the Urals and the ilmenite-magnetite deposits of the Bushveld complex in South African Republic, described above, are the examples of unique vanadium deposits containing vanadium-bearing titanomagnetite ores.

DEPOSITS OF WEATHERING

Deposits of oxidation zone related to polymetallic ores are widely distributed in Africa (Berg-Aunas, Tsumeb, Abenab in Namibia, Broken Hill in Zambia), and also known in Australia, Argentine, Mexico, USSR, USA. As a rule, these are small

deposits of vanadium which concentrates only in oxidized ores (up to 5.6%). Primary sulfide ores contain vanadium in small quantities $(0.00n\text{-}0.0n\%)$. Ore bodies have a pipe-like shape, with the upper part composed of oxidized ores containing cerussite, smithsonite, malachite, azurite, anglesite and the minerals of vanadium, i.e. descloizite, cuprodescloizite and vanadinite. The depth of oxidation zone of such ores usually does not exceed a few hundred metres. Sometimes, the ores occur at deeper levels, which may be explained by groundwater circulation along deep-seated structures of increased porosity.

PLACER DEPOSITS

Large coastal-marine placers of vanadium-containing titanomagnetite sands are known in New Zealand (reserves around 800 thousand tons with 0.7% of V_2O_5). Similar placers are known in the USSR at the Black and Caspian Sea coasts and on the Kurile Islands.

SEDIMENTARY DEPOSITS

The highest content of vanadium (up to 0.22%) is known in Permean sheet-like phosphorites of the Rocky Mountains (USA). Vanadium is produced as a by-product from the wastes of phosphorite processing.

Carnotite and roscoelite deposits in variegated sediments (aleurolites, sandstones, gravellites, and conglomerates) of the Mesozoic sedimentary cover (the type of "Colorado Plateau") are known in many countries. However, they have the highest importance in the USA, where high vanadium contents (up to 1.7%), increased contents of uranium (0.18-0.34% of U_3O_8) and copper (about 0.5%) are observed.

Increased vanadium contents are also noted in high-sulphur grades of oil produced in the Ural-Volga province, Venezuela and Iran. Patronite in asphaltite has been successfully mined in a unique deposit of this type in Minas Ragra (Peru). The deposit is represented by a vein-like body of asphaltite of the length reaching 1 km and the thickness from 8 to 12 m which occurs in Cretaceous shales, sandstones and limestones. Vanadium contents in the run-

of-the-mine ore is about 6%, and up to 36% in the ash.

A considerable amount of vanadium concentrates in a number of sedimentary deposits of iron ores, bauxites, coals and carbonaceous-siliceous shales. Oölitic brown iron ore of the Lorraine (France, FRG, Belgium, Luxembourg) and Kerch (USSR) basins contain 0.05-0.1% of V_2O_5. Increased content of vanadium pentaoxide (0.1-0.2% V_2O_5) is also known in bauxites of Italy, Yugoslavia, India, in coals of Great Britain, USSR and USA, and in carbonaceous-siliceous shales of the Kara Tau ridge (USSR).

METAMORPHOGENIC DEPOSITS

OTANMÄKI. This ilmenite-magnetite deposit is located in Finland and confined to amphibolites occurring in granite-gneiss. The amphibolites have two zones of lenticular ore bodies composed of ilmenite-magnetite ores with average vanadium content of 0.62%. The magnetite concentrate produced here yields 1 300-1 500 tons of vanadium annually.

WILSON-SPRINGS. This deposit in the USA is confined to the zone of argillization on the contact of nepheline syenites and crystalline schists in ancient metamorphic strata. The main concentrators of vanadium (0.6% in average) are clay minerals. It is possible that an enrichment of clay minerals in vanadium was influenced by weathering of metamorphosed rocks. Vanadium reserves in the deposit are estimated to be about 30 thousand tons. Annual production is 2.5 thousand tons.

REFERENCES TO "FERROUS METALS" SECTION

Betekhtin, A. G. Commercial Manganese Ores in the USSR. Moscow, Acad. Sc. of the USSR publishers, 1946.

Borisenko, L. F. Vanadium (Mineralogy, Geochemistry and Types of Endogenic Deposits). Moscow, Nedra, 1973.

Borisenko, L. F. Deposits of Titanium. Deposits of Vanadium. In: *Ore Deposits in the USSR*. Vol. 1, 2nd ed., Ed. Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Chiatura Manganese Deposits. Moscow, Nedra, 1964.

Evaluation of Iron Ore Deposits During Exploration. Moscow, Nedra, 1970.

Geological Structure and Iron Ores of the Krivoi Rog Basin. Moscow, Gosgeolizdat, 1957.

Geology and Genesis of Precambrian Ferruginous, Siliceous and Manganese Formations of the World. *Proc. of International Symposium.* Kiev, Naukova dumka, 1972.

Industry Requirements to the Quality of Mineral Raw Materials, Issues 15, 24, 59, 63, 73, Moscow, Gosgeoltekhizdat, 1960-1963.

Iron Ore Deposits of the Altai-Sayan Mountain Area. Moscow, Acad. Sc. of the USSR publishers. Vol. 1, b. 2, 1959.

Iron Ore Deposits of Kazakhstan and the Ways of Their Development. Moscow, Acad. Sc. of the USSR publishers, 1960.

Khalilov Deposits of Complex Iron Ores. Moscow, Acad. Sc. of the USSR publishers, 1942.

Kholodov, V. N. Vanadium (Geochemistry, Mineralogy, and Genetic Types of the Deposits in Sedimentary Rocks). Moscow, Nauka, 1968.

Leonenko, I. N., Rusinovich, I. A., Chaikin, S. I. Geology, Hydrogeology and Iron Ores of the Kursk Magnetic Anomaly Basin. Vol. 3, Moscow, Nedra, 1969.

Magnetite Deposits of the Kustanai Region and the Ways of Their Development. Moscow, Acad. Sc. of the USSR publishers, 1958.

Malyshev, I. I. Regularities of Formation and Distribution of Titanium Ore Deposits. Moscow, Gosgeolizdat, 1957.

Marsden, R. Y. Iron Ore Deposits of the Superior Lake In: *Ore Deposits of the United States, 1933-1967.* The American Institute of Mining, Metallurgical and Petroleum Engineers, Inc. Vol. I. New York, 1968.

XIX Congres Geologique International Symposium sur les Gisements de Fer du Monde, tome I. Alger, 1952.

Nikopol Manganese Ore Basin. Moscow, Nedra, 1964.

Oölitic Brown Iron Ores of the Kustanai Region and the Ways of Their Development. Moscow, Acad. Sc. of the USSR publishers, 1956.

Pavlov, N. V., Grigoryeva, I. I. Chrome Deposits. In: *Ore Deposits of the USSR.* Vol. 1, 2nd ed., Ed. Acad. V. I. Smirnov. Moscow, Nedra, 1978.

Pavlov, N. V., Kravchenko, G. G., Chuprynina, I. I. Chromites of the Kempirsai Pluton. Moscow, Nauka, 1968.

Pervago, V. A. The Aldan Iron Ore Province. Moscow, Nedra, 1966.

Platform Magnomagnetite Formation. By G. S. Momazi, A. Ya. Akhipenkova, V. F. Kozlov, V. A. Pavlov. Moscow, Nedra, 1976.

Placer Deposits of Titanium in the USSR. Moscow, Nedra, 1976.

Precambrian Iron Ore-Formations of the World. Edited by Skinner Lancaster, USA, 1973.

Sokolov, G. A., Grigoryev, V. M. Iron Deposits. In: *Iron Ore Deposits of the USSR.* Vol. 1, Moscow, Nedra, 1978.

Sokolov, G. A. Chromites of the Urals, Their Composition, Conditions of Crystallization and Occurrence Features. Moscow, Acad. Sc. of the USSR publishers, issue 97. The series of iron ore deposits, 1948.

The Kerch' Iron Ore Basin. V. A. Arbuzov, L. G. Bobrushkin, A. U. Litvinenko et al, Moscow, Nedra, 1967.

The Main Iron Ore Deposits of Siberia. Novosibirsk, 1970. *Proc. of SNIIGGIMS,* issue 96.

Varentsov, I. M., Rakhmanov, V. P. Deposits of Manganese. In: *Ore Deposits of the USSR.* Vol. 1, Moscow, Nedra, 1978.

NONFERROUS METALS

The metals that come as basic elements into nonferrous metallurgy, such as aluminium, magnesium, nickel, cobalt, copper, lead, zinc, tin, tungsten, molybdenum, bismuth, antimony, and mercury, are called nonferrous.

6 ALUMINIUM DEPOSITS

N. Beketov, a Russian chemist, back in 1865 produced aluminum by its substitution for magnesium in molten cryolite (Na_3AlF_6). The method found industrial application in Germany and France at the end of the 19th century.

After the invention of the method of cryolite-alumina melts electrolysis, which had been concurrently made in France by P. Eru and in the United States by Ch. Hall in 1886, and after the development of the hydroalkali alumina production process by K. Byer in Russia in 1887, new favourable conditions have emerged in the world for an expansion of aluminum production industry. In order to obtain alumina from low-grade bauxites the method of sintering is used which has been developed by the Soviet and American production engineers.

Aluminium, because of its light weight (specific weight is 2.7), high electric conductivity, improved corrosion stability and sufficient mechanical strength (particularly in the alloys with Cu, Si, Mg, Mn, Zn, Ni, etc.), has found a broad application in the aircraft (alate metal), automobile and electrotechnical industry, transport, construction, as well as in the industry producing household utensils.

Total reserves of bauxites in capitalist and developing countries, as estimated by 1975, constituted 17.6 billion tons, 90% being concentrated in a tropical zone; 75% of the total reserves fall to Australia, Guinea, Cameroon, Brazil and Jamaica.

Twenty eight countries in the world produce bauxites. In 1975 both capitalist and developing countries produced 63 million tons of bauxites, 80% fall to Australia, Jamaica, Guinea, Surinam, Guyana, Greece and France. Alumina production in capitalist and developing countries in 1975 reached the level of 22 million tons, 10 million tons being aluminium products. The prices for bauxites in 1975 varied from 10 to 20 US dollars, those for aluminium varied from 600 to 700 US dollars per ton.

The pre-revolutionary Russia had no aluminium industry. In the USSR a large-scale production of alumina and aluminium has been created on the basis of cheap electric power supply from powerful hydroelectric power stations and on the basis of a number of discovered deposits of bauxites. For the first time in the world practice the Soviet experts have developed the method of aluminium and its alloys production from high alumina rocks, such as kyanite, sillimanite and andalusite schists.

Polish technologists have proved that there is a possibility to produce alumina on industrial basis from kaolin clays containing around 25% of Al_2O_3 and 3% of FeO. In 1973 in the Federal Republic of Germany the economic feasibility of alumina production from the North Sea red silts

excavated from the sea bottom was proven on the basis of pilot plant tests.

Very large deposits (unique by their size) of bauxites are those having over 500 million tons of reserves, large deposits have from 500 to 50 million tons, small deposits have the reserves less than 50 million tons.

Al_2O_3 contents in bauxites for alumina production should not be lower than 40% (GOST 972-74, Soviet Standard), alumina-silicon ratio must be over 2.6. Bauxites containing Al_2O_3 above 43%, with S and P_2O_5 below 0.3 and 0.5% respectively, with alumina-silicon ratio exceeding six and alumina-lime ratio above 250 are used for production of electro-corundum. Bauxites with alumina-silicon ratio more than two are used for manufacture of high-quality refractory bricks and as fluxes in open-hearth furnaces. High-grade bauxites (Al_2O_3 more than 50% and Al_2O_3/SiO_2 more than 10) are used in production of rapid-setting portland cement.

GEOCHEMISTRY AND MINERALOGY

Aluminium is represented in the nature by only one isotope ^{27}Al. The crustal abundance (clarke) of aluminium is 8.05%. The clarke of its concentration is low and equals 5.

Under endogenous conditions aluminium tends to concentrate in alkali nepheline- and leucite-bearing rocks, and in anorthosites. It also accumulates in the processes of alunitization related to hydrothermal alteration of acid volcanics. The highest accumulations of aluminum are recorded in the residual and redeposited weathering crusts over acid, alcaline and basic rocks.

In the sedimentation processes alumina is dissolved and migrates only in acidic (pH less than 4) or strong alkali (pH more than 9.5) solutions. Precipitation of aluminium hydroxide starts at pH = 4.1. In the presence of SiO_2 the solubility of Al_2O_3 increases, whereas in the presence of CO_2 it reduces. Colloidal alumina is less stable in comparison with colloidal silica and starts coagulating faster than silica thus predetermining a separation of the two

compounds in the course of their joint migration.

Since geochemical mobility of aluminium, iron and manganese compounds are different they tend to separate in the coastal zones of sea reservoirs. Bauxites tend to precipitate closer to the coast whereas iron ores accumulate in the upper part of the shelf, and manganese ores – in its lower part.

Aluminum is found in the composition of over 250 minerals, however commercial importance nowadays is attributed to the following minerals: boehmite and diaspore $Al_2O_3 \cdot H_2O$ (85% of Al_2O_3), gibbsite (the same as hydrargillite) $Al_2O_3 \cdot 3H_2O$ (65.4%), nepheline $KNa_3 [AlSiO_4]_4$ (34%), leucite $K[AlSi_2O_6]$ (23.5%), and alunite $KAl_3[SiO_4]_2(OH)_6$ (37%). Also promising in terms of aluminium extraction are kyanite, sillimanite, andalusite, dawsonite and kaolinite.

The most important ores for aluminium production are bauxites, i.e. the rock containing aluminium hydroxides, oxides and hydroxides of iron, clay minerals, quartz, which has the Al_2O_3/SiO_2 ratio no less than 2. In terms of mineral composition bauxites are distinguished as diaspore, boehmite, gibbsite and complex bauxites containing 2 or 3 above minerals. In terms of structure the bauxites can be stony, loose, oölitic, bean-like, brecciform, jaspery. Bauxites are normally coloured by iron oxides in various shades of red and brown. There are also bauxites of white, grey, green, black and other colours. The bauxites offer high adsorption capacity and constantly contain admixtures of V, Cr, Ca, Ti, etc.

Amorphous alumina which comes as a component of commercial minerals containing aluminium is subjected to ageing with time. As a result, it transforms into boehmite, while the latter turns into gibbsite. Therefore the most widespread type of bauxites in the nature is gibbsite bauxite.

METALLOGENY

The most favourable conditions for creation of bauxite deposits in the framework of a geologic cycle have appeared twice: in the early stage of geosynclinal cycle when geosynclinal deposits were created, and in

the platform cycle, when lateritic and sedimentary deposits were formed.

According to G. Kirpal and V. Tenyakov (1978), in the history of the earth's crust evolution one may identify 12 epochs of bauxite formation:

(1) Late Proterozoic-Cambrian (Western and Eastern Siberia, Altai, China);

(2) Late Ordovician (Central Kazakhstan);

(3) Middle Devonian (Northern Urals, Salair);

(4) Late Devonian (Western slope of the Urals);

(5) Early Carboniferous (Northern American platform, Russian platform, Tikhvin, Northern Onega, Timan, Belgorod districts);

(6) Middle-Upper Carboniferous (Central Asia, China);

(7) Permian (China, North Korea);

(8) Triassic (Northern and Southern Urals, Central Asia, Vietnam, Yugoslavia);

(9) Jurassic (Central Asia, Russian platform, Romania, Turkey, Greece);

(10) Cretaceous (Hungary, Italy, France, Greece, Turkey, Ukraine, Asian part of the USSR: Turgai, Southern Siberia, Central Siberia districts);

(11) Paleogene (Turgai district in the USSR, Australia, Tasmania, Southern and Northern America);

(12) Neogene-Quaternary with the largest deposits containing 80% of the reserves in foreign countries (Jamaica, Dominican Republic, Haiti, Australia, India, the countries of Equatorial Africa).

TYPES OF COMMERCIAL DEPOSITS

All commercial deposits of bauxites are related to exogenous formations. They are classified as the deposits of weathering and sedimentation. The deposits of weathering can be subdivided into residual and redeposited, whereas the sedimentary deposits can be subdivided into those occurring in terrigenous strata of platform regions and those related to carbonate sediments of geosynclinal provinces.

DEPOSITS OF WEATHERING

Bauxite deposits of weathering are subdivided into residual lateritic and residual redeposited.

Residual Lateritic Deposits

Laterites are the products of a deep chemical weathering of alumosilicate rocks of basic, intermediate and acidic composition produced under tropical and subtropical conditions as a result of an intensive and durable leaching of a alkali and silica by warm rain water and simultaneous accumulation of free oxides of aluminum iron and titanium. The lateritic deposits, particularly of Cenozoic tropical regions, have a very great commercial value. In the USSR buried lateritic deposits of bauxites in the ancient weathering crusts have been revealed within the Belgorod district, KMA (Vislovsk and other) and the Ingulets-Dnieper district (Vysokopolsk and others).

BOKE (Guinea). This deposit is the largest deposit of bauxites in the world. It is located 135 km off the coast of the Atlantics in the north-western part of Guinea. Bauxites in the deposit are found in the hilly elevations (bovals) bordered with river valleys with the depths down to 100 m. Bauxite laterites developed as a result of an intensive weathering of the Silurian graptolitic schists during the Paleogene-Neogene time under the conditions of a poorly eroded peneplane. The thickness of the lateritic weathering crust is 10-15 m. Bauxites crop out and are overlain as a rule by ferruginous laterites (red cap).

The deposit is known to have over 100 bauxite bovals arranged in the form of a zone having the north-eastern strike. The length of the zone · is 130 km, width 30-60 km, and its area is over 3 500 km^2 (Fig. 25).

Two different types of bauxites, i. e. eluvial and diluvial, can be distinguished at the deposit in terms of conditions of formation and occurrence, as well as structural and textural features. Both types intermittently substitute each other, being closely genetical and spatial interconnected.

The eluvial bauxites are represented by
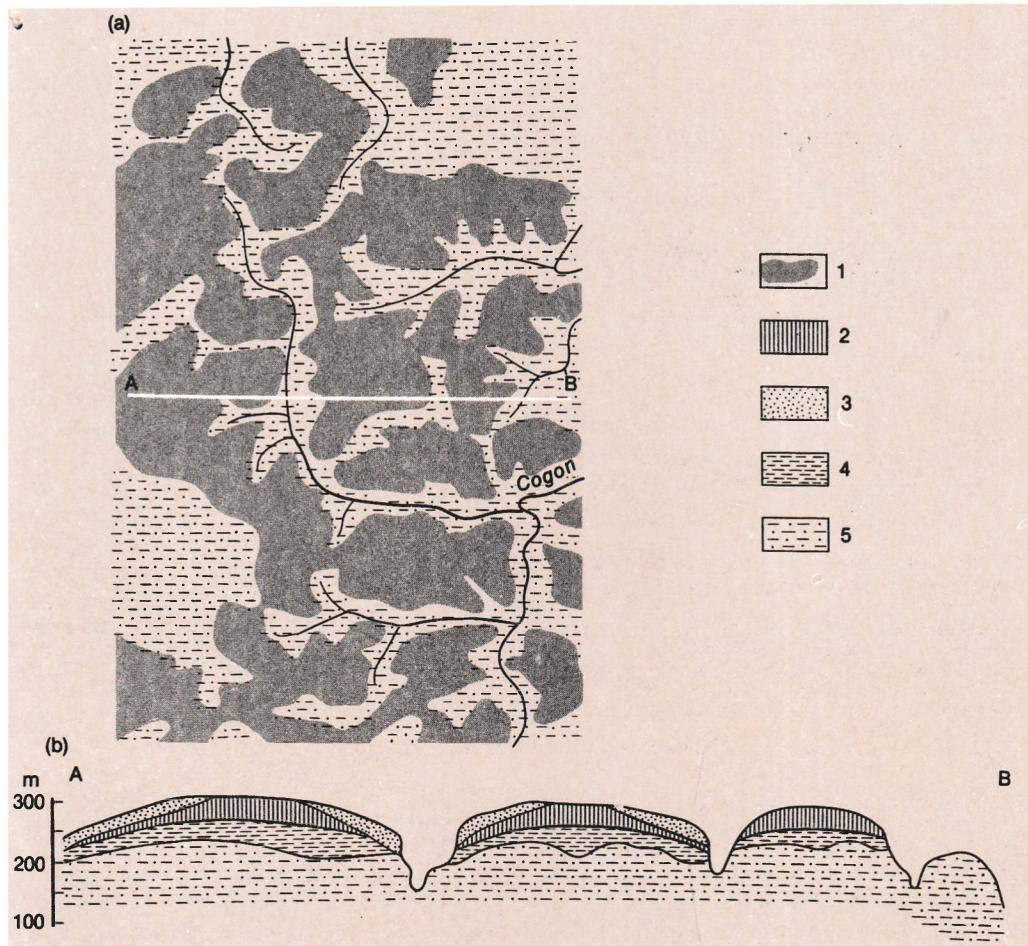
Fig. 25. Schematic map (a) and section (b) of bauxite beds in the Boke deposit (Guinea). (After I. Dubovskaya and B. Odokii):

1 – bauxite beds;
2 – structural bauxites;
3 – fragmental bauxites;

4 – allites, kaolin clays;
5 – graptolitic shales and other terrigenous Ordovician rocks

dense stony ores having a massive, banded or shale structure. They normally constitute the topmost part of the laterite weathering crust. In the lower part of the bauxite-bearing layer there are sometimes loose and earthy varieties of bauxite. The diluvial bauxites are represented by angular or subangular fragments of the eluvial bauxites, having the size from a few to 15 cm. The fragments are cemented by a pelitic, aleuritic, or psammitic material produced at the expense of destruction of the eluvial bauxites.

The main ore-forming minerals of bauxites are gibbsite and hematite with the admixture of boehmite (up to 10%), kaolinite (2-3%), and titanium minerals in the top parts of the deposit. The colour of the bauxites is normally light rose, brown or reddish-brown, the structure is brecciform, conglomeratic or porous. These bauxites are characterized by high concentration of alumina (51-62%), low contents of silica (1-2%), as well as of iron oxides (2-6%) and titanium oxides (2-3%). At marginal content of alumina 50%, total reserves of the deposit mineable by opencast method constitute around 3 billion tons.
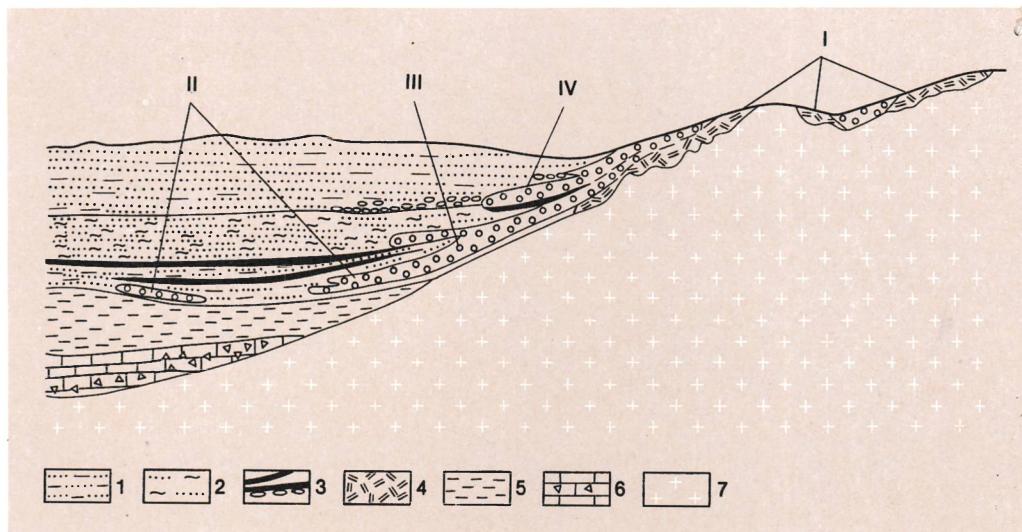
Fig. 26. Generalized section of the most important types of bauxite deposits in Arkansas (USA). (After M. Gordon):

1-4 — Lower Eocene sediments:
  1 — quartzose clays;
  2 — kaolinite clays with interbeds of lignite and lenses of quartz sand;
  3 — bauxites;
  4 — kaolinite clays;
  5 — kaolinite clays and quartz aleurolites of Paleocene;

  6 — limestones, sands and sandstones of Paleocene;
  7 — nepheline syenites of Upper Cretaceous.
Types of bauxite deposits:
  I — laterite;
  II — diluvial-proluvial;
  III — alluvial (bedded);
  IV — conglomerate

Residual Redeposited Deposits

This type of deposits is represented by the deposits in Arkansas region (USA), Australia and Guiana coastal plain (Guyana, Surinam and Guiana). On the territory of the USSR no similar deposits are known.

ARKANSAS DEPOSITS. The basement of the region is composed of Paleozoic clayey sandstones and shales, which have been gently folded. In the Cretaceous age the structure of Paleozoic rocks was intruded by the batholites of nepheline syenites. Early in the Eocene epoch these batholites were projected on the surface of land in the form of hills having up to 180 m height. The formation of kaolinite and bauxite weathering crusts occurred in nepheline syenites during the pre-Tertiary time. The content of Al_2O_3 in nepheline syenites is 18-21%, whereas in bauxites it is over 32%, silica content in nepheline syenites is 56-60%, which in bauxites is up to 12%. In the Tertiary epoch bauxites were partially eroded and redeposited on top of sandy-clayey Eocene sediments overlying

the massif of nepheline syenites (see Fig. 26).

Residual (lateritic) bauxites are found in the summits or mid parts of the hills composed of nepheline syenites being separated from the latter by a horizon of kaoline clays up to 10 m thickness. In the upper part they have a concretionary structure, whereas in the bottom part the structure looks like one of nepheline syenites. Diluvial deposits of bauxites occur at the foots and in the lower parts of the hill slopes are overlain by kaoline clay of 90-m thickness. The upper part of the deposits is composed of bauxites having a concretionary structure, whereas bauxites of the lower part have a clay structure. There are also conglomeratic bauxites made up of the fragments of clay and bauxites produced as a result of mechanical motion of massive bauxites.

Alluvial bauxites are composed of pebble and fragments of bauxites and occur in bauxite-kaoline diluvial sediments. They have a diagonal · and horizontal bedding
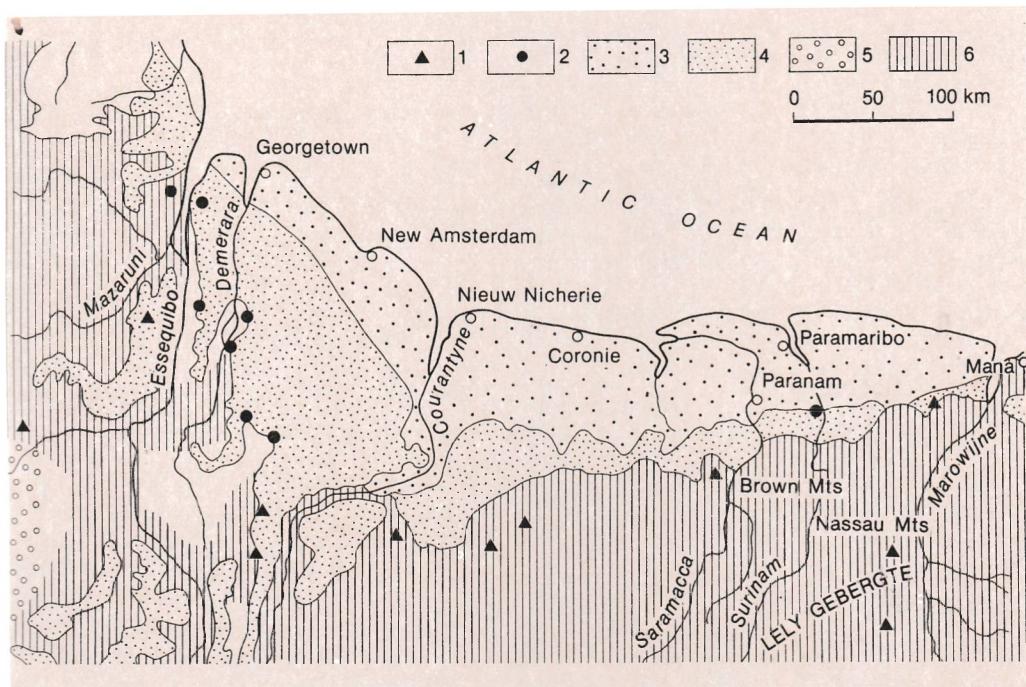
Fig. 27. Schematic geological map of bauxite deposits in the Guiana coast (Guyana, Surinam, Guiana). (After D. Kersen):

1 – lateritic bauxites;
2 – sedimentary bauxites;
3-5 – sedimentary rocks of Mesozoic and Cenozoic:
3 – clays with interlayers of sands and coquina;

4 – sands with interlayers of clay and bauxites;
5 – sandstones with interlayers of conglomerates;
6 – granodiorites, basalts, metamorphic rocks of the Precambrian basement of the Guiana shield

which indicates that they were formed under river, lake and marsh conditions. The bauxites are underlain and overlain with clays, which contain lenses of lignite, and turn into these clays down the slope.

The deposits of bauxites have been revealed on the area of around 700 km². The size of the single deposit varies from fractions of a hectare to a few hundred hectares. In terms of reserves the deposits vary from a few hundred tons to a few million tons. The thickness of bauxite beds and lenses in large deposits varies from 3 to 10 m, reaching sometimes 20 m.

Bauxites may be greenish-grey in colour passing over to brown shades. In terms of mineral composition they are classified as a gibbsite type. They reveal also the presence of kaolinite, hematite, goethite, siderite, magnetite, pyrite, ilmenite, sphene, anatase and rutile. Depending on the content of kaolinite, the chemical composition of the bauxites varies (in w.%) such as Al_2O_3 32-62; SiO_2 2-12; iron oxides 1-9%; loss of ignition at the expense of H_2O, CO_2 and other volatiles amounts to 15-32. The reserves in the deposit are estimated as 50 mln tons.

THE DEPOSITS OF THE GUIANA COASTAL PLAIN. Multiple deposits in Guyana, Surinam and Guiana form a bauxite-bearing province elongated along the Atlantic coast over the distance of 600 km with the width of 100-150 km (Fig. 27). The deposits in the Guiana are confined to the northern slope of the Guiana shield which is composed of granites, diorites and metamorphosed sedimentary and volcanic Precambrian rocks. On top of the ancient basement sandy-clayey sediments of Mesocenozoic are developed.

Lateritic bauxites occur at the flattened summits and slopes of gently sloping hills of the ancient basement with the heights up to

30-35 m that bordering the coastal plain. The thickness of the bauxite bed-like deposits is 12 m.

In the sandy-clayey rocks there are redeposited alluvial bauxites of Tertiary age. The thickness of these lenticular deposits is up to 10 m. The high-grade bauxites are confined to the central part of the bauxite beds. In the bauxite-bearing sediments one finds horizontal stratification, lenses and interlayers of coaly clays and lignites. The bauxites of very high grade contain from 58 to 66% of Al_2O_3 at minimal silica and iron oxides content (0.1-2.5%). Total bauxite reserves in the province are estimated as 850 million tons.

THE DEPOSITS OF AUSTRALIA. The largest deposits of bauxites with the reserves estimated as over 1/4 and production of 1/3 of the world's total are known in the Northern and South-Western Australia. They are represented by sheet deposits of the area of hundreds of square kilometres (Fig. 28). The bauxite deposits are located in the area of developed lateritic cover overlying Precambrian metamorphic and igneous rocks (the deposits of Wape, Gove), basaltic and pyroclastic rocks (Mitchell plateau), dolerites and shales (Darling range). In the bauxite-bearing series one can usually distinguish two or three horizons from 2 to 15 m thick that are mainly composed by pisolitic, pebble, gravel, brecciform bauxites cemented by a looser material of the same chemical and mineral composition that of fragmental bauxites.

The grade of the bauxites is very high and in average they contain (in w.%) Al_2O_3 50-62; SiO_2 3-5; Fe_2O_3 12-20; TiO_2 3-4; loss of ignition is 20-26. In terms of mineral composition they are normally gibbsitic with a subordinate quantity of boehmite. The presence of hematite, magnetite, kaolinite, diaspore, anatase, corundum, and quartz in the bauxites is noted.

The bauxite deposits were formed as a result of redeposition over small distances, and, possibly, subsequent bauxitization of products of the lateritic weathering crusts in Late Cretaceous and Early Tertiary epochs. The process stopped in the Late Tertiary cycle as a result of the uplifting of the region.

SEDIMENTARY PLATFORM DEPOSITS

Sedimentary platform deposits of bauxites are confined to the marginal portions of syneclises, troughs between the outcropping parts of ancient rocks, erosion-tectonic depressions and valleys that often develop in the junction zones between platforms and their fold fringe. They occur in the continental deposits of mainly lake-bog facies and often are related to coal-bearing sediments. In the profile they are usually located above the bauxites and at a rather large distance from projections of the basement in comparison with bauxites.

The Visean bauxite deposits of the East European platform that are located in the Western and Northern peripheral zones of the Moscow syneclise (Tikhvin, North-Onega, Middle-Timan and Southern-Timan districts) could serve as the examples of such deposits. The deposits of this type of the Carbonaceous and Permian ages are also known in the Chinese and North American platforms.

In the south-western part of the Siberian platform and in the Yenisei ridge (Chadobets, Tatarsk and Priangarsk districts), as well as in the Turgay trough (Amangeldinsk, West-Turgay and Central Turgay districts) the bauxite deposits are confined to the areas of carbonaceous rocks of the folded basement. Their formation occurred in the Cretaceous and Paleogene time in karstic sinkholes, contact-karstic and karstic-depression troughs.

TIKHVIN GROUP OF DEPOSITS. This group of deposits is located in the belt of Lower carboniferous sediments in the north-western limb of the Moscow syneclise. The bauxite-bearing zone is elongated in submeridional direction over the distance of 260 km. Within the limits of the zone there have been found over 30 deposits. The premineral basement of the Tikhvin group of deposits is composed of sandstones, micaceous shales with sand lenses and colour variegated sandstones of the Upper Devonian age.

The bauxite-bearing sediments lay in disconformity on colour variegated clays of Devon and are confined to the mid part of
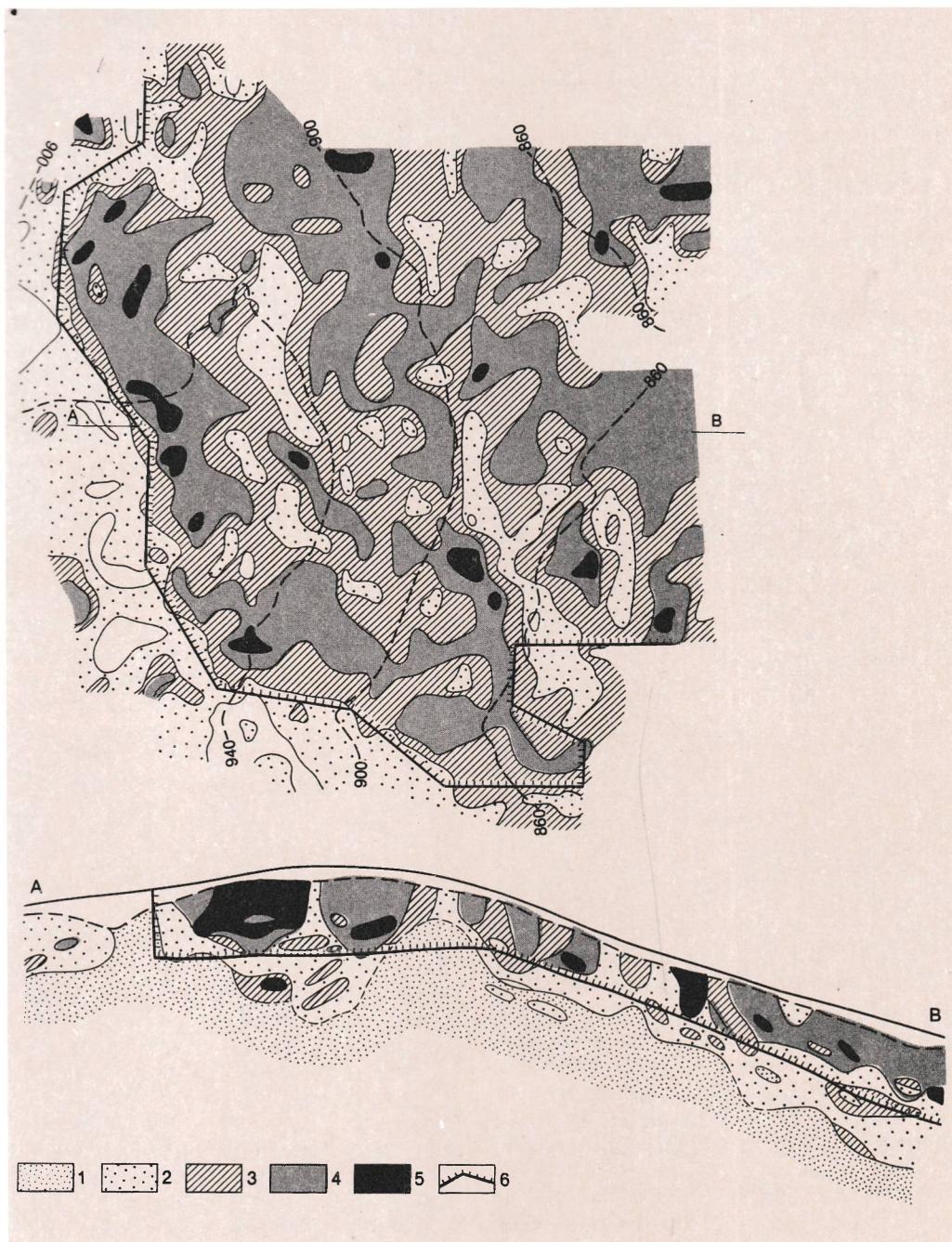
Fig. 28. Geological plan and section showing distribution of bauxites in the Darling Range deposit (Australia). (After G. Baxt):

Content of AL(%):

1 – < 20;
2 – 20-25;
3 – 25-30;

4 – 30-35;
5 – > 35;
6 – the boundary of the ore body
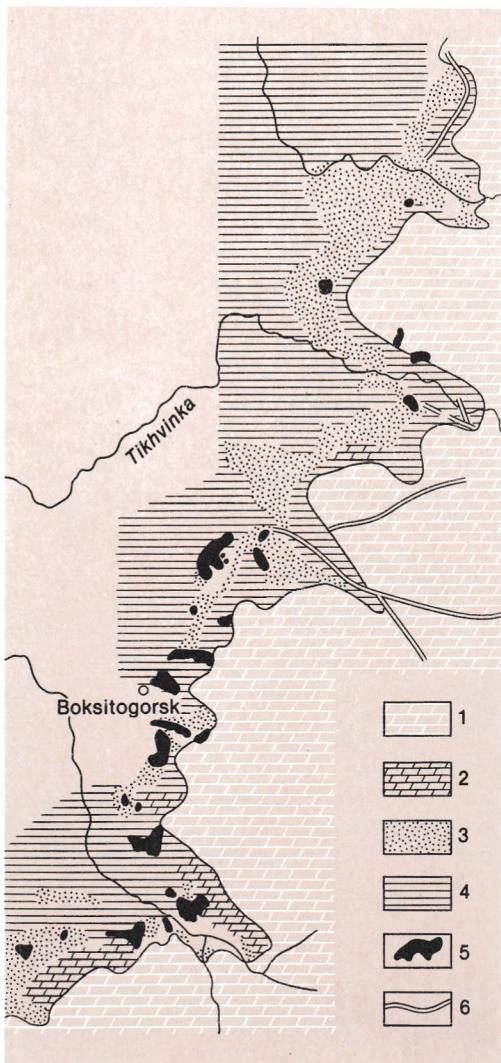
Fig. 29. Scheme of the geological structure of the territory of the Tikhvin bauxite deposits group. (After S. Vishnyakov and L. Kalnin):

1 – limestones of the Serpukhov suite;
2 – limestones of the Oka suite;
3 – sandy-clayey deposits of Lower Carboniferous;
4 – sandy-clayey sediments of Upper Devonian;
5 – bauxite deposits;
6 – direction of Paleovalleys filled with coastal-delta sediments

the Tula horizon in Lower Carboniferous. The bauxite-bearing rocks are overlain by colour variegated clays with lenticular inclusions of sands, and in some cases with boulder clay and other glacial sediments or a sandy-vegetation layer. The rocks of the Tula horizon are overlain by the Lower Carboniferous sandy-clayey rocks with interlayers of limestones and more seldom dolomites. Above them Quaternary clays and loams are located.

The premineral relief, developed on ancient sediments, is represented by a wide elevation elongated in meridional direction and dissected by river valleys, and wide and deep canyons. The length of such valleys varies from 1 to 7 km, width being from 0.1 to 1 km, depth 10-40 m.

The commercial bauxite deposits in the area are found in ravine valleys and depressions of the premineral relief. They have narrow elongated lenticular form with flattened slightly concaved or rough roof surface and convexed downward foot (Fig. 29). The bauxite beds occur at the depth reaching 100-150 m, but usually being no more than 40 m.

Bauxites of commercial grade are located in the central part of the profile across the bauxite deposit, whereas toward peripheral parts they are substituted by allites (bauxite-like rocks with alumina-silica ratio less than 2.6) and siallites (kaolinite rocks containing no free alumina with alumina-silica ratio close to 1). Because of this, the contents of alumina and iron oxide gradually increase, while that of silica decrease from periphery to the core of the deposit. The Devonian clay weathering crust served in the locality as a parent rock for bauxite formation.

The bauxites have characteristically reddish-brown colour, almost no bedding, poorly pronounced grading of fragmental material, high concentration of vegetation residues and secondary calcite. Among the bauxites one can identify stony, loose, and clayey varieties. In terms of structural properties they can be fragmental, oölitic-bean and finely dispersed (pelitic). In terms of mineral composition the bauxites can be classified as a gibbsite-boehmite-kaolinite type. They contain (w.%) Al_2O_3 36-49; SiO_2 11-18; Fe_2O_3 10-19; TiO_2 2-3; CaO 1-10; alumina-silica ratio in individual deposits may vary from 2.8 to 4.1.

SOUTHERN-TIMAN GROUP OF DEPOSITS. The oldest formations in this area are
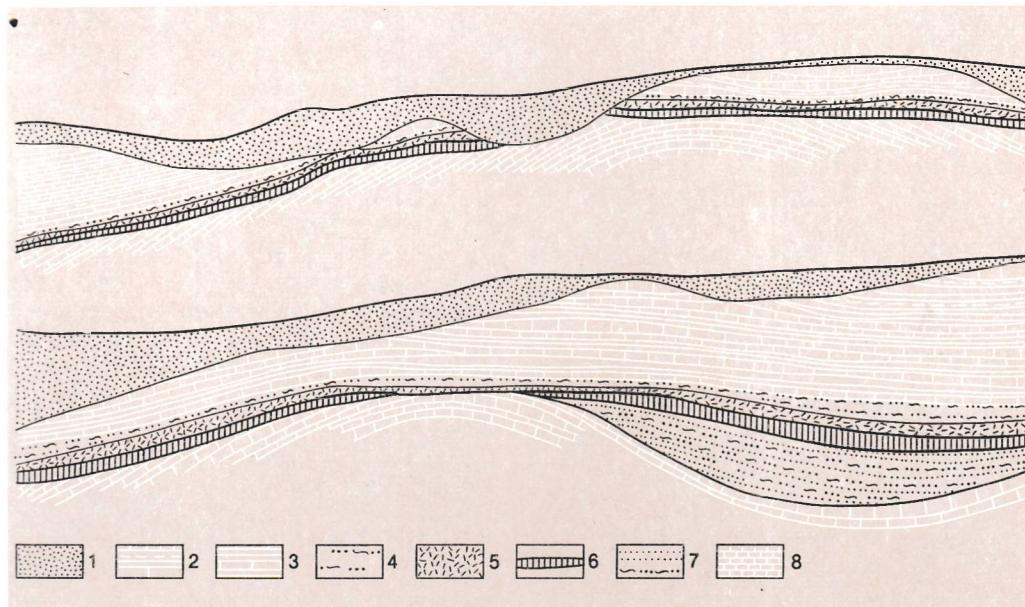
Fig. 30. Schematic geological sections of the deposits in Southern Timan. (After J. Krylov):

1 – Quaternary sediments;
2-7 – sediments of Middle and Lower Carboniferous:
  2 – clays with limestone interlayers;
  3 – limestones with clay interlayers;
  4 – sandy-clayey;
5 – coal-bearing;
6 – bauxites;
7 – sands with clay interlayers;
8 – limestones with interlayers of Upper Devonian clay

represented by carbonate rocks and shales which belong to the metamorphic series of the Riphean age. Those rocks are overlain, with a sharp angular unconformity, by almost horizontal sandy-clayey and carbonate (limestones, dolomitized limestones and dolomites) rocks of the Devonian, Carbonaceous and Permian systems, that are almost completely overlain by Quaternary loams and loamy sands.

The bauxites are related to terrigenous sediments of the Lower Carboniferous Tula horizon (Fig. 30). They overlay carbonate and carbonate-argillaceous rocks of Upper Devonian or their diluvium being covered by the carbonate sediments of the Visean age up to 70-m thickness. Sometimes bauxite deposits are found in karstic zones which develop in limestones. They have an elongated shape with a winding lower surface of the stratum. Ore deposits have considerable area but their thickness is low (up to 2-5 m). Two-three beds of bauxites and related rocks were found in the section within some parts of deposits. Coarser

fragmental allites and bauxites occur at the base of bauxite-bearing rocks, in the middle part of the strata there are pelitic bauxites, whereas in the topmost part oölite-bean-fragmental allites and kaoline clays with the admixture of coalified vegetation residues are located. There were local sinkings accompanied by the repetition of sedimentary rocks' sequence as the depressions were filled by a bauxite material. Such a composition of the section is explained by this fact and the accumulation of coalified vegetation (bogging) ended the sedimentary rocks sequence.

In terms of mineral composition the bauxites are related to kaolinite-gibbsite-boehmite and kaolinite-boehmite types, the first is developed in the north-western part of the deposit, whereas the second in the south-western part of it. In terms of lithologic composition argillite- and stony-like varieties which have grey colour, and massive, brecciform or oölitic structure can be identified. Less distributed are argillaceous greyish and yellowish-white

bauxites. Pelitic and metacolloidal texture in the middle part of the stratum is substituted by the oölitic-bean-fragmental texture at the bottom and top of the section.

In terms of chemical composition the bauxites are characterized by high content of alumina and silica, low content of ferric oxide and often high content of sulphur. They contain (w.%) Al_2O_3 40-70; SiO_2 12-28; Fe_2O_3 4-13; S 0.4-3. Silica ratio varies from 2.6 to 3.2.

SEDIMENTARY GEOSYNCLINAL DEPOSITS

The sedimentary geosynclinal deposits of bauxites are confined to the middle and marginal parts of geosynclinal troughs, more precisely to the zones of their junction to platforms. They occur mainly in the bends close to the marginal parts of large-size anticlinoria and median massifs, that in the period of bauxite formation represented islands, or considerable areas of a dry land. They were formed in shallow waters during the intermissions in the processes of marine sediment accumulation, and were always located above the surface of unconformity. Often such bauxites occur on the karstic surface of limestones of reef origin. The karstic caves acted as traps where bauxites were accumulated and stored, being protected from subsequent denudation.

Toward the centre of depressions and projections of the premineral relief bauxites wedge out, gradually transforming into variegated clays or becoming divided into several interlayers. The bauxite beds and

Fig. 31. Schematic geological and lithological map of the premineral pre-Eifelian basement and bauxite-bearing sediments in the North-Ural bauxite-bearing province. (After G. Kirpal):

1 – the area of bauxite-bearing sediments, both discovered and potential;
2 – barren zones;
3 – light-grey and rosy massive reef limestones;
4 – massive and bedded dark-grey limestones, bituminous shales, sandstones and conglomerates;
5 – basalt, plagioclase and pyroxene-plagioclase porphyrites;
6 – conglomerates, sandstones, and sandy-clayey shales;
7 – shales, porhyrites, tuff sandstones, sandstones, basaltic tuffs;
8 – tectonic faults

enclosing rocks are usually folded and metamorphosed.

Weathering crusts of the elevated basic volcanics, schists and other rocks located close to the karstic caves acted as a source of bauxite formation. In the coastal-marine regions of explosive volcanic activity the karstic caves on reef plateaus, according to C. Goldich (in the case of Jamaica and Haiti) and A. Kalugin, were filled with volcanic ash which as a result of weathering was transformed into bauxite. In the scientific community there are advocates of a volcanogenic sedimentary origin of geosynclinal bauxites in the zones of either vigorous submarine (A. Peive) or land (K. Zelenov) volcanic activity which is accompanied by leaching of alumina from volcanic and sedimentary rocks by solfataras and fumaroles.

The bauxites in geosynclinal regions are characterized by high and persistent quality. Among these diaspore-boehmite, diaspore and boehmite varieties are dominating, whereas slightly dislocated deposits contain gibbsite.

The deposits of this kind occur in the North-Urals, South-Urals, Salair and Bokson bauxite-bearing regions of the USSR, as well as in Hungary, Greece, France, Yugoslavia, Jamaica, Haiti and Dominican Republic.

THE NORTH-URAL BAUXITE-BEARING REGION. In this region Ivdel', North-Urals and Karpinsk groups of deposits are known (listed from north to south). The North-Urals group is the main one in the region and consists of Krasnaya Shapochka, Kal'ya, Novokal'ya, Cheryomukhovo, Sos'va and Vsevolodo-Blagodatskii deposits. They are all confined to a flat meridional depression composed of Middle Silurian and Devonian limestones and shales (Fig. 31). The bauxites lay on a denudated karsted limestone surface of Lower Devonian. The roof of the bauxites is flat and represented by bituminous limestones and marls (Fig. 32).

Within the bauxite-bearing zone steep faults and upthrows with the amplitudes of displacement reaching 200-400 m are developed. The largest of these have a sublatitudinal strike and, as a rule, serve as
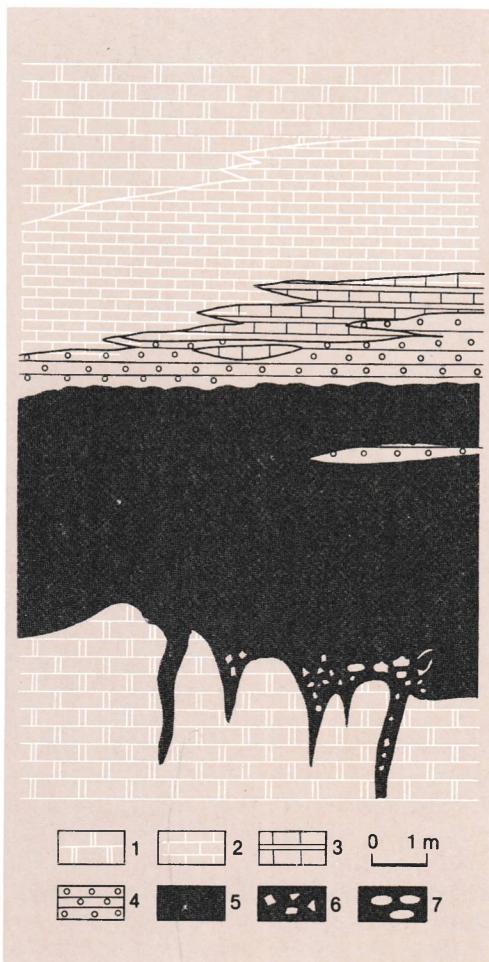
Fig. 32. Generalized geological column of the Devonian bauxite deposits in the Northern Urals. (After G. Bushinsky):

1 – limestones of light-grey colour, massive;
2 – dark-grey limestones;
3 – marls with interlayers of limestones;
4 – grey, banded bauxites with marine fauna;
5 – red bauxites;
6 – limestone fragments in bauxite;
7 – limestone gravel in bauxite

a delineation boundary between different deposits.

Bed-like bauxite deposits dip eastward at the angles of 25 to 45°. The ore horizon can be subdivided into two subhorizons, the lower, containing red soiling, non-soiling and jaspery bauxites, and the upper one, containing variegated pyritized bauxites. The red soiling bauxites fill karstic caves in the limestones, whereas red non-soiling and
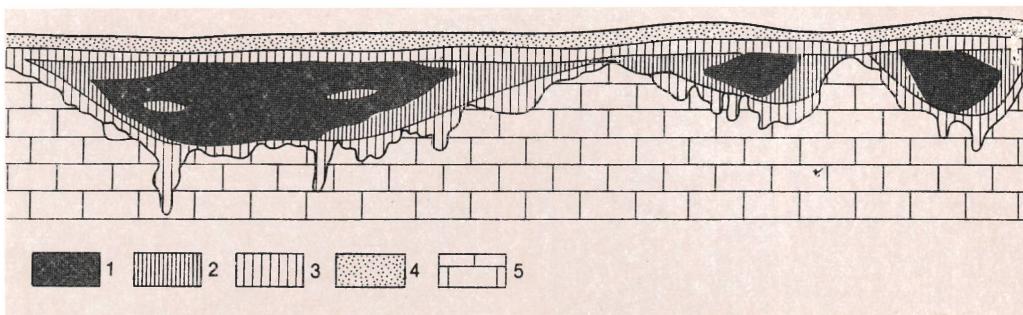
Fig. 33. Schematic geological section of the Mazy deposit in France. (After I. Valeton):

1 – bauxites;
2 – bauxite clays;
3 – kaolinite clays;

4 – manganous-ferruginous crust;
5 – limestones

jaspery bauxites tend to accumulate on the slopes of depression. Variegated bauxites are developed everywhere. The thickness of the red bauxites varies from a few centimetres to 20 m and occasionally more. The thickness of variegated bauxites reaches 3 m with the average of 0.5-0.7 m.

In terms of the mineral composition red bauxites are classified as diaspore, whereas jaspery and variegated bauxites as diaspore-boehmite. The bauxites structure is bedded and bean-like. The red bauxites are characteristically of a high grade, containing (w.%) Al_2O_3 53-55; SiO_2 2-6; Fe_2O_3 23-25; CaO 1.6-2.5; S 0.1-0.4 (up to 1%); CO_2 1.9-3.6; TiO_2 2-2.5. They constitute 85-97% of the total reserves of the deposits.

THE DEPOSITS OF SOUTHERN FRANCE. A bauxite-bearing belt stretches along the Mediterranean Coast over 400 km, its width being 60 km. Bauxites occur in the depressions of the karsted surface of Lower Cretaceous limestones (Barremian, Aptian), being overlain by sandy-clayey sediments of Upper Cretaceous (Senomanian-Danian) and Eocene ages (Fig. 33). Bauxites are typically of Albian-Aptian age. The ore deposits have a bed-like or lenticular shape of 5 to 20 m thick (in karstic cavities it may reach 100 m) and of up to 10-30 km long. The lower part of the deposits is composed of ferruginous red bauxites, whereas upward in the section they are gradually substituted by bauxites of rosy, grey and white colours. The bauxites are of diaspore, boehmite or gibbsite-boehmite compositions. Their texture is aphanitic, pisolitic, bean-oölitic, the

structure being banded. The bauxites are high grade. The run-off-the-mine bauxites contain (w.%) Al_2O_3 55; SiO_2 2-6; Fe_2O_3 20-25; TiO_2 2-3. Total reserves of the high grade bauxites are estimated as 100 mln tons.

THE DEPOSITS OF JAMAICA. The bauxite deposits of Jamaica are covering the Middle Eocene-Lower Miocene limestones that discordantly lie on the Lower Eocene and Cretaceous basement (Fig. 34). The most intensive karsting occurred in the Middle Miocene time when the main stage of the bauxite formation began. The karstic relief and the boundaries of karstic depressions have determined both shape and size of the bauxite deposits. Large-size bauxite deposits are confined to large elongated cup- and basin-shaped depressions in the areas of limestone development. Occasionally they occur in the zones of tectonic faults where the most intensive karstification takes place. Small deposits fill cones, tubes and cavities of irregular form on the slopes of cavernous limestone uplifts. Bauxites occur above the ground and karstic water table and are overlain by a thin soil layer.

Over 100 commercial grade bauxite deposits are known altogether on Jamaica. Their size varies within broad limits, ranging from small pockets to gigantic ore bodies stretching up to 30 km. The thickness of the ore bodies may vary from a few tens of centimetres up to 30 m. The average commercial thickness of the deposits is 3-10 m.

In terms of mineral composition the bauxites are classified as boehmite-gibbsite (1 : 3)
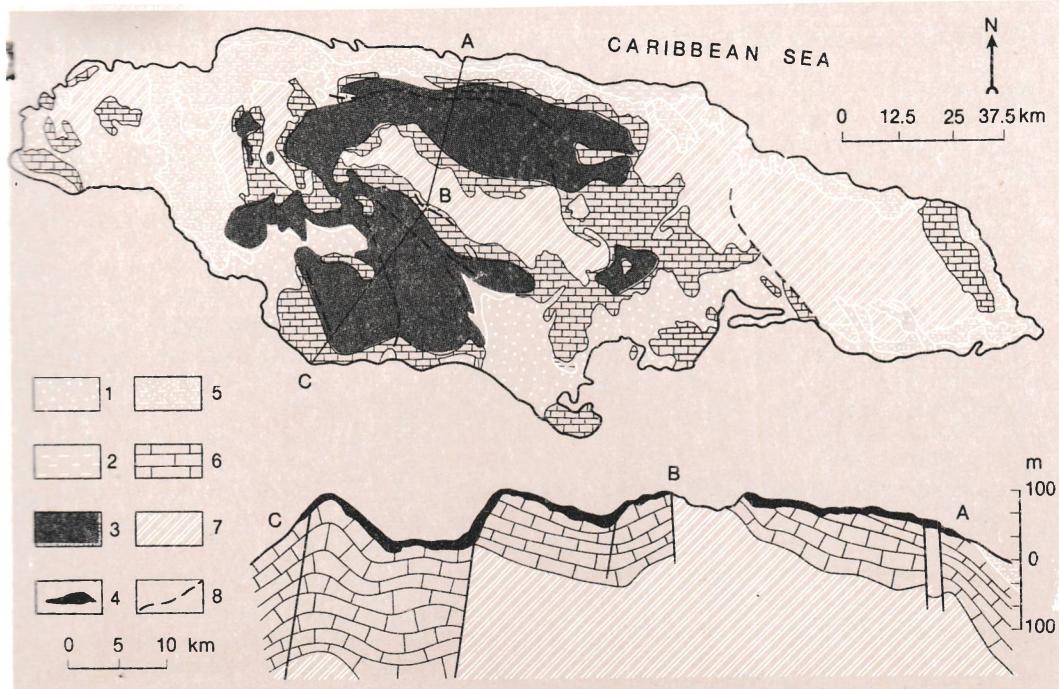
Fig. 34. Geological map and section of the Jamaica island. (After D. Komer):

1 – alluvial deposits;
2 – limestones and terrigenous rocks;
3 – bauxites and bauxite-bearing formations of Miocene-Quaternary age;
4 – bauxite deposits;
5 – marly limestones of Medium and Upper Miocene;

6 – Middle Eocene-Lower Miocene limestones, enclosing bauxite beds;
7 – igneous, metamorphic and terrigenous rocks of the Cretaceous and Lower Tertiary age;
8 – tectonic faults

with hematite, goethite, kaolinite and halloysite. Their colour is typically red, reddish-brown and yellowish-brown. They could be consolidated or earthy. Average content of the main components in the bauxites is (w.%): Al_2O_3 45-50; SiO_2 0.5-3.5; Fe_2O_3 17-23; TiO_2 2-3; P_2O_5 0.3-3; CaO 0.1-1.2; loss of ignition 26-28. The high concentration of iron oxide and phosphorus pentoxide does not allow to regard the bauxites as of a high grade. The bauxite reserves, however, are believed to be great (total reserves make around one billion tons), they occur close to the earth surface and therefore are of a great commercial value.

NON-BAUXITE ALUMINIUM RAW MATERIAL

In the USSR to produce alumina and aluminium other sources than bauxites are used, such as nepheline concentrates of the apatite-nepheline ores from the Khibiny deposit (the Kola Peninsula), nepheline ores from the Kiya-Shaltyr (the Kuznetsk Alatau) and Tezhsar (the Armenian SSR) deposits, as well as alunite ores from the Zaglik deposit (the Azerbaijan SSR). Moreover, a number of nepheline deposits have been explored and developed for production in the Eastern Siberia, Central Kazakhstan and Tadzhik Republic, as well as deposits of alunite ores in the Uzbek Republic, Ukraine and Far East.

Good potentials for manufacture of silicon-aluminium alloys and aluminium are offered by the alumina high kyanite schists in the Cave group (the Kola Peninsula) and by the kaoline clays in the Angren deposit (the Uzbek SSR).

7 MAGNESIUM DEPOSITS

As the first metallic magnesium was produced by a French chemist A. Bussy in 1829, the use of the metal on industrial basis has begun late in the 19th century. The magnesium alloys with aluminium, zinc and manganese have characteristically high strength and light weight.

The world production of metallic magnesium now makes around 300 000 tons per year. Half of this amount is produced from dolomite while the second half comes approximately equal from magnesite, sea water and brines. The production of magnesium from dolomite has been developed in France and United Kingdom, from magnesite in the United States, France and Federal Republic of Germany, from brines in the USSR and USA. The price for magnesium in the world market is 2 300 US dollars per ton.

The crustal abundance (clarke) of magnesium is 1.87%, its average content in sea water is 0.13%. Magnesium is one of the most light weight metals, its specific weight being 1.74. Out of 3 isotopes of magnesium (^{24}Mg, ^{25}Mg, ^{26}Mg) the most widespread in the nature is the isotope ^{24}Mg.

The main types of magnesium raw material are: dolomite $CaMg(CO_3)_2$ (13.1%), magnesite $MgCO_3$ (28.7%), carnallite $MgCl_2 \cdot KCl \cdot 6H_2O$ (8.7%), bishofite $MgCl_2 \cdot 6H_2O$ (11.9%) and sea water. Magnesite which is applicable for metallic powder production must contain no less than 43% of MgO, no more than 2.5% of CaO and 2% of SiO_2.

Deposits of dolomite in carbonate formations of sedimentary origin are widely distributed and their reserves are enormous. Deposits of magnesite were mainly formed under the mesothermal conditions as a result of metasomatic replacement of limestones and dolomites by magnesian solutions and as a result of interaction of hot solutions containing CO_2 with ultrabasic rocks. Accumulations of cryptocrystalline (amorphous) magnesite were also formed as a result of weathering of ultrabasic rocks.

The deposits of magnesite are known in the USSR in the Urals (Satkin, Beloretsk, Katav-Ivanov groups of deposits) in the Irkutsk region (Savinsk, Onotsk), the Krasnoyarsk region (Udereisk), the Eastern Kazakhstan (Ushcharyshkh) and in other areas. Large deposits of magnesite are known in Austria, Greece, Czechoslovakia, Yugoslavia, North Korea, China, Canada and USA.

Magnesian salts are known in great quantities in salt deposits of the lakes in Kazakhstan, in the waters of the Aral and Caspian Seas. The deposits of mineral carnallite of sedimentary origin are known in the salt occurrences in the USSR (Verkhnekamsk in the Urals, Solegorsk in Byelorussia, etc.), German Democratic Republic, France, Spain and other countries.

THE VOLGOGRAD DEPOSIT. This unique deposit of bishofite is known in the salt basin of the Caspian Sea syneclise occurring in the Kungurian layer of the Lower Permian system. Bishofite has been found within salt strata in association with carnallite, kieserite, sylvite and halite. In some areas bishofite occurs as almost entirely monomineralic deposit (mineral content being 88-96%), with the thickness 10-40 m, sometimes reaching 100-200 m. Within the limits of the Volga region monocline the presence of four beds of bishofite has been established, at the depth of 1 000-1 800 m, two of them distributed in a regional scale. The beds of bishofite have been traced by drillholes strikewise over the distance of 400 km, and over 30-40 km across the strike. The area is estimated to have bishofite reserves of more than 200 billion tons. This deposit can be mined by underground leaching.

8 NICKEL DEPOSITS

Nickel is known from the very old times (200 B.C.) when it was used as monetary alloy and for other purposes. The metal was first obtained by a Swedish chemist A. Cronstedt in 1751. Because of its high chemical, thermal and mechanical stability the metal is used in metallurgy (80% of total consumption) to produce stainless steel for jet aircrafts, rocket design, nuclear engineering, radio electronics, energetics, chemical and food industries. Nickel is produced from nickel, copper-nickel, cobalt-nickel ores.

The price for one ton of nickel is up to 2850 US dollars. In 1975 capitalist and developing countries produced 573.5 thousand tons of nickel. World reserves of nickel are: prospected – 59.3 million tons, total – 95.7 million tons. Unique deposits (in New Caledonia; Sudbury in Canada) contain over 500 thousand tons of metal, large ones contain 500-250 thousand tons, medium size 250-100 thousand tons, and small deposits contain less than 100 thousand tons. High-grade sulfide ores contain more than 1% of nickel, regular ores contain 1-0.5%, low-grade ores 0.5-0.1%. High-grade silicate ores contain over 2% of nickel, regular ones contain 2-1.3% and low-grade 1.3-1%.

GEOCHEMISTRY AND MINERALOGY

There are five known stable isotopes of nickel with atomic mass numbers 58, 60-62, 64, the dominating isotope being ^{58}Ni (67.8%). The clarke of nickel is $5.8 \cdot 10^{-3}\%$; the clarke of its concentration being 200. The clarke of nickel increases from acidic $(8 \cdot 10^{-4}\%)$ to basic $(1.6 \cdot 10^{-2}\%)$ and to ultrabasic $(2.2 \cdot 10^{-1}\%)$ magmatic rocks. Correspondingly, commercial concentrations of nickel are mainly associated with basic-ultrabasic magmas, related to subcrustal sources. The presence of sulphur, which as nickel, copper and iron, has a subcrustal source, the metals are fractionated in a form of sulfides.

At high temperatures (1 500-1 200 °C) segregation (liquation) of magma into two immiscible melts, i. e. sulfide and silicate, occurs. The process of liquation is influenced by sulphur concentration, the composition of silicate magma, and in the first run, by quantities of Fe, Mg, and Si, as well as by concentrations of chalcophile elements in the liquid silicate phase. The presence of iron in the silicate melt increases solubility of sulfides by tens of times. Magmatic deposits of sulfide copper-nickel ores formed as a result of crystallization of liquated sulfide melt.

In granitoid magmas in relation to the postmagmatic hydrothermal process a certain concentration of nickel together with cobalt, arsenic, sulphur, and sometimes with bismuth, silver and uranium may take place.

In exogenous conditions nickel accumulates in weathering crusts as a result of chemical decomposition of olivine and serpentine which contain nickel in isomorphic to magnesium form. Nickel then is transported by groundwater in the form of bicarbonate $Ni(HCO_3)_2$ and subsequently precipitated in the lower horizons of weathering crusts.

Forty five nickel minerals are known. Among them the minerals of sulfide ores are: pentlandite (Fe, Ni)S (22-42%), millerite NiS (65%), nickeline NiAs (44%), chloanthite $NiAs_{3-2}$ (4.5-21.2%), polydymite Ni_3S_4 (40-54%) and gersdorffite NiAsS (26-40%). In the silicate nickeliferous ores the following minerals are known: garnierite $NiO \cdot SiO_2 \cdot H_2O$ (NiO 46%), nepouite $12NiO \cdot 3SiO_2 \cdot 2H_2O$ (20-46%), and revdinskite $3(Ni, Mg) O \cdot 2SiO_2 \cdot H_2O$ (46%). In the zones of oxidized arsenic containing ores one can find annabergite $Ni_3As_3O_8 \cdot 8H_2O$ (37%) which has a value only as an indicator mineral.

METALLOGENY

Nickel deposits are not typical for a geosynclinal cycle. Only rare and commercially insignificant nickel and cobalt sulphoarsenide hydrothermal deposits were formed at that time in relation to granitoids of the middle and late stages. The main proportion of magmatic cooper-nickel sulfide ores was formed at the stage of reactivation of ancient plantforms when rocks of the trap formation, usually represented by fully differentiated gabbro, were originated. Exogenous deposits of silicate nickel ores are confined to weathering crusts, and were formed in a platform cycle.

In the geologic history of the Earth development there are two main epochs of copper-nickel sulfide deposit formation, i.e. Proterozoic (Baltic and Canadian shields, South Africa, Australia) and Kimmerian (Siberian platform). Silicate nickel deposits in weathering crusts were formed in recent time. They are found in the Southern Urals, Brazil, New Caledonia, Cuba, Philippines and Madagascar.

TYPES OF COMMERCIAL DEPOSITS

There are the following types of nickel commercial deposits: (1) magmatic; (2) plutonogenic hydrothermal; (3) weathering crust.

MAGMATIC DEPOSITS

Liquation magmatic deposits of copper-nickel sulfide ores are known in the USSR in the Kola Peninsula (Pechenga, Allarechensk, Moncha), in the Krasnoyarsk region (Talnakh, Oktyabr', Norilsk I), and in other countries: in Finland (Pori), Sweden (Klövsjö), Canada (Sudbury, Thompson), USA (Stillwater), South African Republic (Bushveld, Insizva), and Australia. They all are related to differentiated basic-ultrabasic massifs enriched in magnesium. These stratified intrusives in shields are composed of peridotites, pyroxenites, gabbro, norites and gabbro-diorites of hypabyssal facies, and gabbro-dolerites, dolerites and picrites of subvolcanic facies in the platform sedimentary cover. More basic varieties compose the lower parts of the massifs (their basement), less basic varieties make up the upper horizons.

Ore bodies are located inside, on the periphery at the bottom part and outside, close to parent intrusives. Among them one finds: (1) sheet "hanging" bodies of disseminated ores; (2) sheet and lenticular bottom-close bodies of massive "schlieren" and streaky-disseminated ores that sometimes extend in underlaying rocks; (3) lenses and irregular bodies of contact breccia ores; (4) vein-like and vein bodies of massive ores. The dimensions of the ore bodies vary from a few hundred meters to 1 000-1 500-m-long strikewise, and from a few hundred meters to 800-1 000 m along the dip, the thickness ranging from 1-2 to 40-50 m. Occasionally, the thickness may be as high as 100 m. The ores may be syngenetic which occur as disseminated, rarely as massive, and epigenetic which occur as injected massive and brecciated. Usually the ores are complex and, besides nickel and copper, contain Pt, Pd, Rh, Ru, Co, Se, and Te. The ores have rather regular mineral composition. The main ore-forming minerals

are: pyrrhotite, chalcopyrite, pentlandite; subordinate minerals being magnetite, pyrite, cubanite, bornite, polydymite, niccolite, millerite, violarite, sperrylite and cooperite. The non-metal minerals are represented by olivine, basic plagioclase and pyroxene. Besides, there are also garnets, epidote, serpentine, actinolite, talc, chlorite and carbonates.

The enclosing rocks are sometimes accompanied by thin fringes of actinolite, scapolite, antigorite, chlorite, serpentinite and other hydroxyl-containing minerals. Sometimes the halos of altered, i.e. of skarnified, silicified and carbonatized rocks, may be significant (Talnakh). However, these hydrothermal alterations occurred after formation of the main mass of sulfide copper-nickel ores, that had been formed in the processes of liquation during magmatic stage. This general stage, according to M. Godlevskii (1968), consists of several sub-stages: (1) early sub-stage, during which segregation of a sulfide liquid developed; (2) medium sub-stage, when crystallization of rock-forming silicates (at the temperatures of 1 100-1 200 °C and higher) occurred, but sulfides remained liquid; (3) late hysteromagmatic sub-stage, manifested in crystallization of syngenetic sulfides at sufficiently high temperatures (600-800 °C) and in formation of injected phenocrysts in the enclosing rocks (600-800 °C); (4) final stage, during which the processes of sulphurization and injection of vein sulfide melt took place. Here ore melt evolved to water sulfide-bearing solution, and late bornite-millerite ores were precipitated. The final low-temperature stage of the postmagmatic process is also responsible for a limited redeposition of the ores.

As a certain limiting value of the nickel content in the ore was reached as a result of gradual evolution of the sulfide melt composition during its separation and crystallization, the further evolution consisted in an increase of the concentration of copper at the expense of iron (Fig. 35). It is substantiated by the pseudoternary $FeS - Ni_2S_2 - Cu_2S$ system in Fig. 36. It follows from the diagram that the crystallization of sulfide ores begins with a solid solution of pyrrhotite and develops along peritectic

nes, the next product being pentlandite and then chalcopyrite.

THE TALNAKH-OKTYABR' GROUP OF DEPOSITS. This group of deposits is located in the Krasnoyarsk region, on the north-western margin of the Siberian platform. The area of the deposit is composed of the platform sedimentary cover formations (upwards), such as terrigenous-carbonate and halogenic rocks of Devonian, coal-bearing terrigenous sediments of Permo-Carboniferous (Tungus series), and tuff-lavas of Permo-Triassic. These rocks make up the Kharayelakh trough in the south-western centrocline of which the Talnakh and Oktyabr' deposits are situated. The synclinal trough is cross-cut by the Norilsk-Kharayelakh deep-seated fault. The rocks in the area have a gentle dipping (angles are 10-15°) in the northern directions.

The deposits are confined to the interformational Talnakh basic-ultrabasic intrusive of a complicated structure. It consists of the independent massifs – branches, which merge in the north-east of the territory where a magma channel-way is supposed to be. These branches have sheet-like and trough shapes assuming a cross-cutting position from the base of the tuff-lava strata to the Devonian carbonate-clayey sediments. The Talnakh deposit is located in the upper ore horizon and is connected to the North-Eastern, Central and South-Western intrusive branches which developed in the form of bands with the thickness of 200-250 m (Fig. 37). The Oktyabr' deposit is located in the lower ore horizon and is confined to the North-Western, Kharayelakh and Lesnoozyorsk branches occurring in the Devonian rocks.

The ore-bearing differentiated intrusions related to hypabyssal facies of trap volcanism have the anisotropic structure. The stratified Talnakh instrusive contains the following horizons (upwards): (1) contact and taxitic dolerites; (2) picritic dolerites; (3)olivine dolerites; (4) olivine-free dolerites; (5) gabbro-dolerites and quartz-containing dolerites; (6) leucocratic gabbro, gabbrodiorites and eruptive breccia. The intrusive was formed from a sole magmatic melt as a result of crystallization-gravitational differentiation. First, olivine segregated
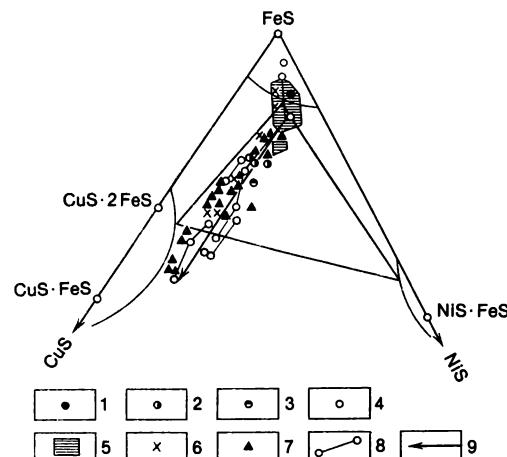
Fig. 35. Standard composition of Norilsk sulfide ores. (After M. Godlevsky):

1-3—average composition:
  1—of vein ores;
  2—of segregation disseminated ores;
  3—of injected disseminated ores;
4—pyrrhotite lenses;
5—field of vein ores;
6—injected disseminated ores;
7—chalcopyrite veins;
8—differentiation trend of copper veins;
9—general line of crystallization and infiltration evolution
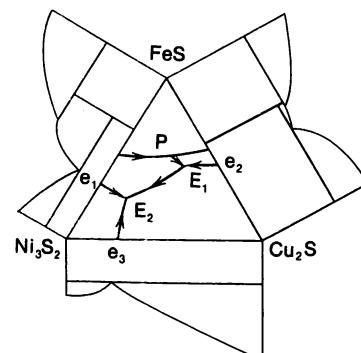
Fig. 36. Schematic phase diagram of the pseudo-ternary system $FeS-Ni_3S_2-Cu_2S$ (projection on a base plane). (After G. Popova and V. Yershov):

P—peritectic point;
e—points of a binary eutectic;
E_1 and E_2—points of a ternary eutectic. Arrows show the general trend of crystallization of the sulfide meit

(at the temperature 1 200 °C) and accumulated in the bottom part of the intrusive. Next, plagioclase crystallized (1 170-1 140 °C) followed, after some delay, by pyroxene (1 140-1 100 °C). Finally, quartz crystallized from the residual melt (1 070-1 060 °C).
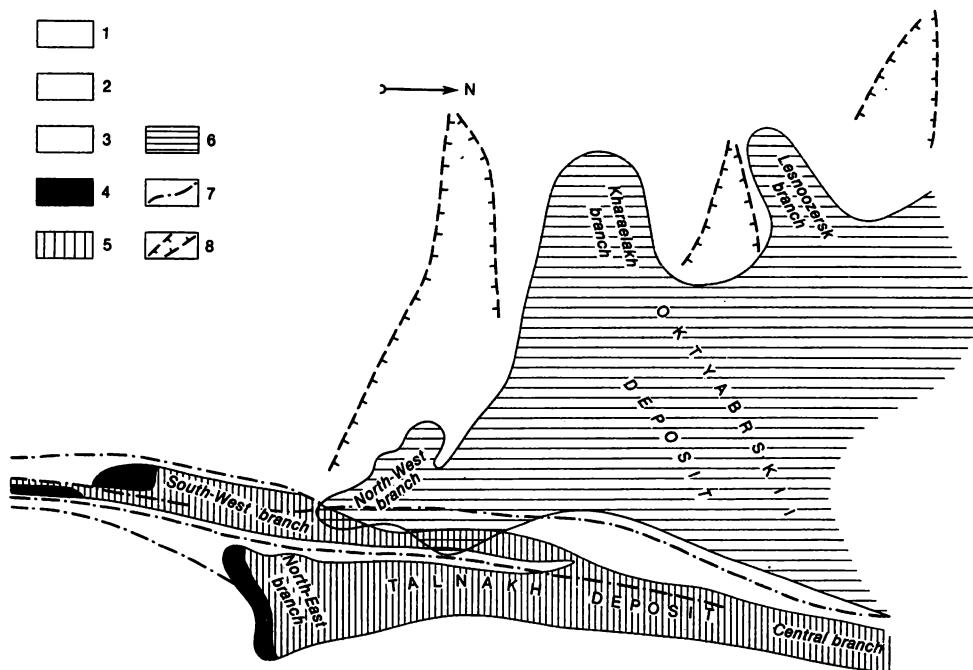
Fig. 37. Schematic map of the Talnakh ore field structure. (After V. Kravtsov):

1 – Middle-Lower Paleozoic carbonate-marly deposits;
2 – terrigenous sediments of the Tungus series (C_3-P);
3 – volcanogenic strata of Lower Triassic;
4 – outcrops of the ore-bearing intrusion under Quaternary sediments;
5 – the distribution area of the branches of the "upper" ore horizon;
6 – the same for the "lower" ore horizon;
7 – tectonic seam of the Central graben;
8 – fissure-block subsided structures

Five ore-bodies of sheet-like and lenticular forms related to five different intrusive branches are known in the Talnakh and Oktyabr' deposits. They consist of spatially adjacent bodies composed of disseminated, streaky-disseminated and massive ores. The main ore-bearing differentiates are picritic, taxitic and contact dolerites that constitute around 10% of the intrusive thickness. The contours of the deposits repeat, in general, contours of the intrusions. The main mass of the ores accumulates in the zone of the lower endo- and exocontact of the massifs. Sometimes only disseminated and massive ores occur at the roof of the intrusions.

Three commercial types of the ores can be distinguished: (1) disseminated (77% of the total mass of the ore); (2) massive sulfide ores in the bottom area (10%); (3) streaky-disseminated ores (13%) in the rocks of exocontact. Pyrrhotite, cubanite and chalcopyrite-talnakhite ores with variable concentration of pentlandite, also milerite-bornite-chalcopyrite and pyrite ores are developed.

Main ore minerals are pyrrhotite, pentlandite and chalcopyrite; subordinate minerals being cubanite, magnetite, ilmenite, titanomagnetite. Rare minerals are pyrite, millerite, bornite, talnakhite, valleriite, heazlewoodite, troilite, covellite, godlevskite and platinum group minerals. The structures of the ores can be massive, brecciform, disseminated, streaky-disseminated and mottled. The textures can be porphyritic, hypidiomorphic-granular, xenomorphic-granular, subgraphic, interstitial, drop-shaped, sideronitic, flame-shaped, loop-shaped and latticed.

The zonality of the disseminated ore deposits is manifested in succession of a vertical direction from the roof of picritic gabbro-dolerites to taxitic gabbro-dolerites and in a horizontal direction from the central parts to flanks of cubanite-moihukite-troillite associations, that include sulfides incompletely saturated with sulphur, by chalcopyrite-pyrrhotite associations, in which pyrrhotite is often represented by the most sulphur saturated variety.

The internal structure of massive sulfide ore deposits is characterized by a succession, from one flank of the deposit to another, of pentlandite-chalcopyrite ores by pentlandite-chalcopyrite-pyrrhotite-cubanite ores, and then by the ores of the pentlandite-cubanite-chalcopyrite association (Fig. 38). The exocontact streaky-disseminated ores sometimes demonstrate a vertical zonality of minerals, i.e. in upward and downward directions from the intrusion pyrrhotite ores are essentially substituted by chalcopyrite and then by millerite-bornite-chalcópyrite and pyrite ores essentially.

There are two main viewpoints on the problem of formation of sulfide copper-nickel deposits. One of them is magmatic liquation (N. Urvantsev, V. Koṭulskii, M. Godlevskii), and the other is metasomatic (V. Zolotukhin, V. Ryabov). The first viewpoint, which seems to be the most creditable, shows that disseminated sulfide ores in picritic and taxitic gabbro-dolerites were formed as a result of liquation that occurred at the early stage of crystallization of the Talnakh intrusive. Massive ores were formed from the sulfide melt in the bottom part of the intrusive. However, with the progress of crystallization of sulfide melt (800-600 °C), along with the reduction of temperature, according to V. Vortsepnev, the melt evolved to low temperature (450-70 °C) hydrothermal solutions of chloride-sodium-calcium composition, from which an insignificant amount of redeposited and exocontact ores was formed.

SUDBURY. The deposit is located in Canada (Ontario). The area of the deposit is composed of quartzites, granite-gneiss of Archean age and thick strata of Proterozoic rocks (over 10 km). The whole area is divided into metamorphosed volcanogen-
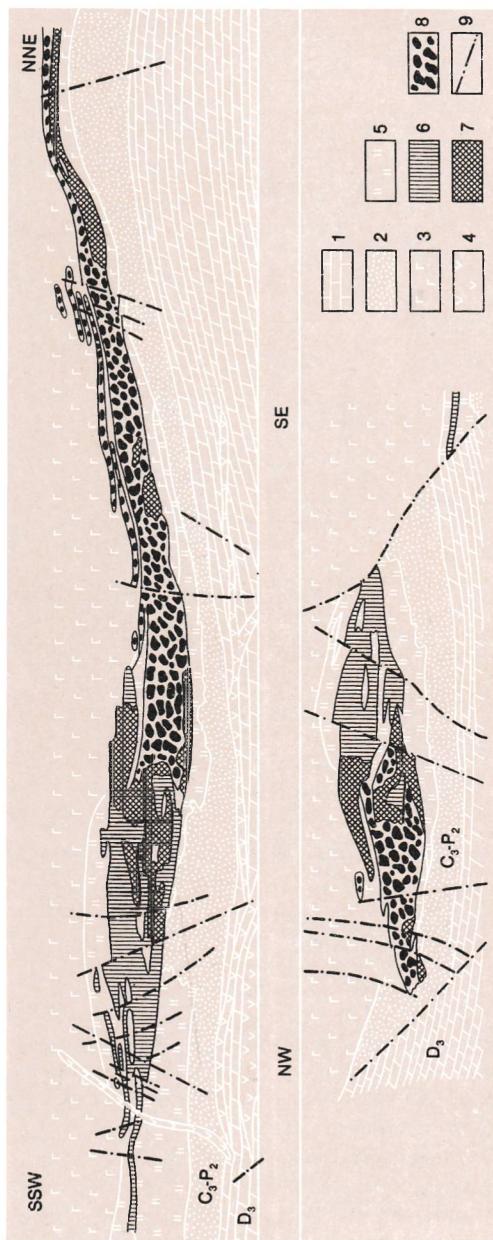
Fig. 38. Scheme of the internal structure of massive ores in the South-Western part of the Talnakh deposit. (After L. Sukhov and V. Izoitko):

1 – dolomites, marls;
2 – sandstones, aleurolites, argillites;
3 – gabbro-dolerites of the Talnakh intrusion;
4 – dolerites of the non-differentiated sills;
5 – contact-altered rocks;
6 – pentlandite-chalcopyrite-pyrrhotite ores;
7 – pentlandite-pyrrhotite-cubanite ores;
8 – pentlandite-cubanite-chalcopyrite ores;
9 – tectonic faults
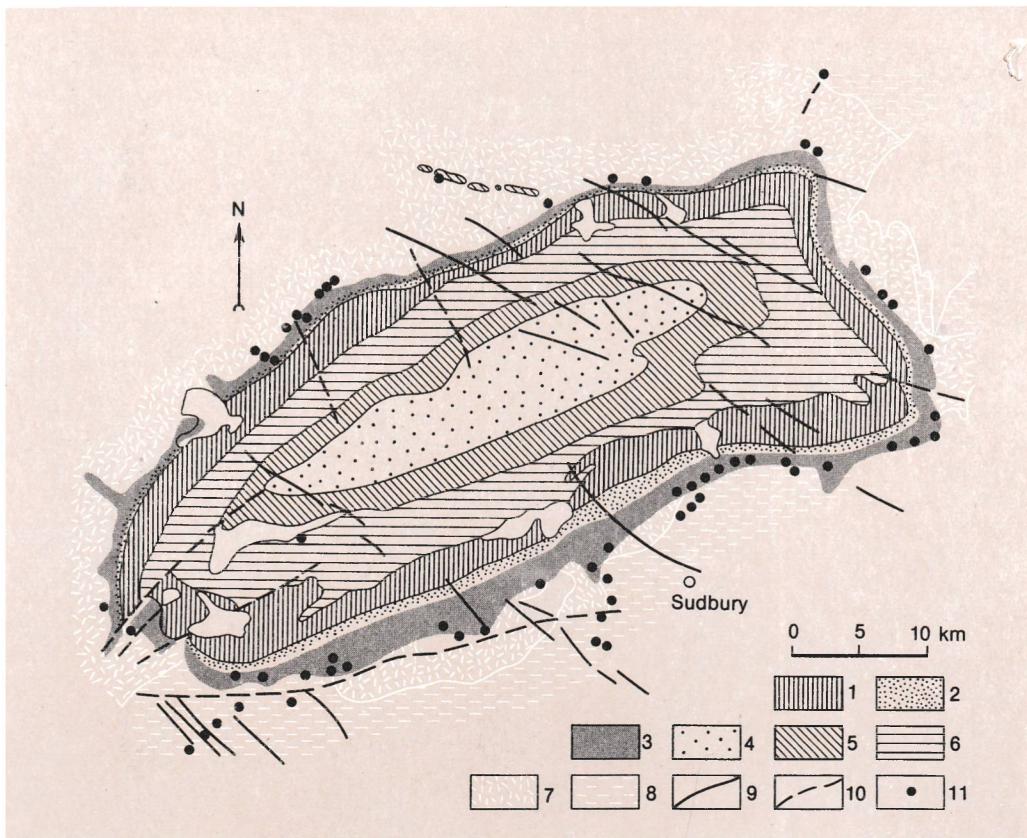
Fig. 39. Schematic geological map of the Sudbury lopolith, Canada. (After F. Grant et al.):

1 – micropegmatites;
2 – quartz gabbro;
3 – norites, quartz diorites;
4 – Chilisford sandstones;
5 – rocks of the Onvatin formation;
6 – rocks of the Onaping formation;

7 – granites and Archean gneisses;
8 – the rocks of Huronic series;
9 – dikes of olivine diabases;
10 – faults;
11 – copper-nickel sulfide deposits

ic-sedimentary deposits of Huronian group and sedimentary rocks (conglomerates, sandstones, shales) of the Whitewater group, which consists of the three formations, i.e. Onaping, Onvatin, and Chelmsford. The Precambrian complexes of the rocks are overlain by a thin platform sedimentary cover made of Paleozoic sediments. The Proterozoic strata form a synclinal trough over an Archean basement. They are complicated by sublatitudinal and submeridional regional faults. At the intersecting points of the faults within the marginal part of the Proterozoic trough an ore-bearing massif called Sudbury (1 700 million years old) is situated. It intruded into the sedimentary strata of the Huronian

and Whitewater group. The massif was formed at the depth of 2-3 km from the surface. In plane it has the oval shape with a long axis striking in sublatitudinal direction over 60 km and a shorter axis of 25 km length (Fig. 39). The massif in the cross-section has a shape of an overturned cone with the top located at the depth of 10-25 km from the surface. The foot of the intrusive has been intersected in the peripheral part by drillholes at the depth of 1.5 km. It has a centroclinal setting with angles of 30-50°. The massif is composed of differentiated series of rocks of the early intrusive phase, i.e. quartzite norites, at the bottom, gabbro-norites, gabbro and quartzite gabbro, substituted by granophyres be-

ing located above them. In the lower part of the Sudbury intrusive there is a sheet-like body of augite norites and hypersthene gabbro of the later intrusive phase associated with eruptive breccia and the dikes of diorites and quartz diorites that cut the underlying series of the footwall rocks.

Ore bodies have sheet-like, vein and lenticular forms (Fig. 40). They border the Sudbury massif on its periphery, sometimes penetrating underlying rocks over a few kilometres. The sizes of the ore bodies are considerable. For example, one of the ore bodies in the Little-Stoby mine has 610-m length along the strike and 730-m length down the dip with the thickness of up to 20 m. Two types of ore can be distinguished. Low grade disseminated ores, which form bottom ore bodies of sheet-like and lenticular shape at the base of early norites, and high grade ores, which compose vein-like injection bodies within late norites, breccias, diorite dikes and underlying rocks. The high grade ores are represented by the fragments of the enclosing rocks cemented by gabbro-norites and sulfides. The main ore-forming minerals are: pyrrhotite, pentlandite, chalcopyrite, and cubanite. The subordinate ore minerals are: magnetite, ilmenite, nickeliferous pyrite, gersdorffite, niccolite, maucherite, heazlewoodite, bornite, valleriite, sphalerite, galena and stannite. The structure of the ores can be massive, brecciform, cellular, disseminated and streaky. The structures could be hypidiomorphic-granular, subgraphic, drop-shaped and latticed. According to A. Greig, magnetite was the first which seggregated from the melt followed by ilmenite, then pyrite and arsenopyrite (about 750 C). Massive crystallization of pyrrhotite began below its stability state (650-600 °C) with a gradual increase of the amount of seggregated pentlandite. By the end of the ore crystallization process chalcopyrite began to accumulate.

There are two main hypotheses regarding the genesis of the Sudbury deposit. The classical one considers the deposit as having a magmatic origin, while a new one, the so-called meteoritic hypothesis, explains the formation of the deposit as a result of collision between a large-size asteroid and
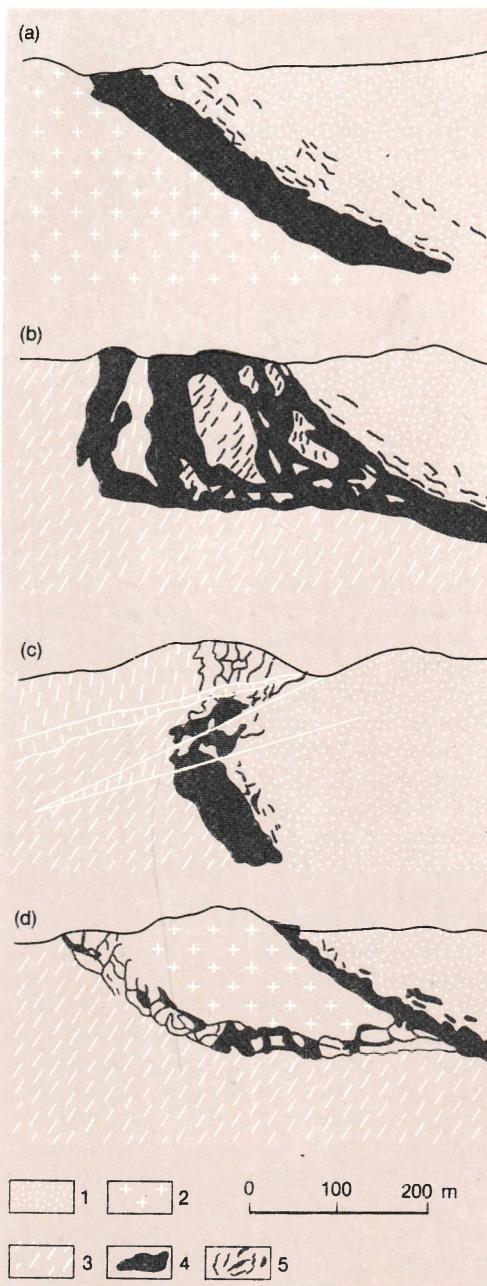
Fig. 40. Typical sections of the ore bodies located close to the margin of the intrusive in Sudbury. (After A. Coleman):

a – fringe ore bodies;
b – dislocated fringe ore bodies;
c and *d* – vein-like ore bodies at the bottom of the intrusive;
1 – norites;
2 – ancient granites;
3 – ancient greenstone rocks;
4 – massive ores;
5 – stringer ores

the earth surface. According to the hypo-thesis about the Sudbury magmatic origin, low-grade disseminated ores in primary massive norites were formed as a result of in situ liquation process. High-grade massive and brecciform ores were formed at a later stage as a result of injection from a deep residual sorce of the liquated silicate-sul-fide melt.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

The plutonogenic hydrothermal deposits of complex ores that contain nickel (Ni-Cu, Ni-Co-Ag, Ni-Pb-Zn, and Co-Ni-Ag-Bi-U) are known in the USSR (Khovuaksy in Tuva), and in other countries such as Mo-rocco (Bu-Azer), Canada (Cobalt, Eldorado), Burma (Boudvin), Czechoslovakia and GDR (Erzgebirge). They are related to moderately acidic granitoids of middle and late stages of a geosynclinal cycle, being associated with the dikes of diabase and diorite porphiries that cut sedimentary of metamorphic strata. Occasionally, nickel-cobalt veins cut serpentinized ultrabasic rocks (Bu-Azer). Ore bodies are typically represented by veins and vein-like bodies. They can be traced over tens and several hundred meters strikewise and over the same distance dipwise, the thickness ranging from 0.1 to 1 m and more, being in average 0.4-0.5 m. The main ore-forming minerals are: niccolite, smaltite, chloantite, skutterudite, safflorite; the principal gangue minerals are represented by quartz and calcite; subordinate ore minerals: glaucodot, arsenopyrite, gersdor-fite, cobaltite, lollingite, chalcopyrite, bornite, sphalerite, galena, native silver, native bismuth, occasionally pitchblende; subordinate gangue minerals: dolomite, rhodochrosite, chlorite, occasionally serpen-tine. The process of mineral formation developed in two or three stages, the minerals of cobalt and nickel crystallized during the early stages, whereas the minerals of silver (sometimes of uranium) in the latest. The enclosing rocks are silicified, sericitized and carbonatized. In some of the deposits a pre-ore skarnification (Kho-vuaksy) and serpentinization (Bu-Azer) can be observed.

Among hydrothermal deposits one car distinguish several ore formations: (1) arse, nopyrite-glaucodot-cobaltite (Bu-Azer in Morocco); (2) smaltite-chloanthite-nickeline (Khovuaksy in Tuva); (3) smaltite-chloan-thite-argentite (Cobalt in Canada); (4) five-metal formation (Ni-Co-Ag-Bi-U) (Eldorado in Canada). Since nickel in the deposits of the above formations is only subordinate metal and is extracted as a byproduct, these deposits have been described in other chapters of the book: "Deposits of Cobalt", "Deposits of Silver" and "Deposits of Uranium".

DEPOSITS OF WEATHERING

Deposits of silicate nickel ores in weather-ing crusts are known in the USSR, in the Urals (Kempirsai, Sakharinsk, Buryktal, Rogozhinsk, Cheremshansk), and in other countries: New Caledonia island, Indonesia, Cuba, Brazil, USA, Australia, Greece, and Albania. The nickel-bearing lateritic weather-ing crusts which developed over massifs of serpentinized ultrabasic rocks of variable age were formed in the Kimmerian and, especially, Alpine epochs. In the course of chemical weathering of ultrabasic rocks, particularly under conditions of a tropical climate, decomposition of olivine and serpentine which contained nickel in iso-morphous with magnesium form was deve-loped. Nickel was freed and transported, often together with cobalt, from the upper horizons of weathering crust to the lower ones. Here, since the alcalinity of infiltrat-ing solutions increased, precipitation of secondary nickel-containing minerals, such as garnierite, nontronite, revdinskite, nepoui-te, and asbolan, occurred.

Among the weathering crusts one can distinguish two types, i.e. kerolith-nontro-nite-ochreous (full profile) and kerolith-ochreous (incomplete profile). Full profile consists of the following zones (down-wards): (1) ochreous-siliceous formations; (2) nontronitized serpentinites; (3) leached serpentinites. The thickness of each zone varies from a few metres to 30-50 m. In incomplete profile the nontronite zone is not present.

In terms of structural and morphological

...tures three types of weathering crusts ...ld be identified: (1) areal (Kempirsai, Sakharinsk in the Urals, and the deposits in ...); (2) linear, or fracture-related, that ...re often found in combination with the first ...re Rogozhinsk in the Urals, the deposits ...New Caledonia); (3) contact-karstic relat-...ed to the tectonic contacts of serpentinites ...nd limestones (Ufalei).

SAKHARINSK DEPOSIT. It is located in the S...th Urals. On the territory of the deposit M...ddle Paleozoic volcanogenic sedimentary ...ks are intruded by the Kuysak gabbro-...roxenite-dunite massif of the Carbonifer-...us age. The rocks are overlain by loose ...diments of Late Paleogene, Neogene and Quaternary. The 15-70-m-thick blanket-like ...eathering crust of Mesozoic-Paleogene ...erlies all the Paleozoic rocks. The crust is ...assified as a full-profile kerolite-...ntronite-ochreous profile consisting of the ...lowing zones (downwards):

1. ochreous-siliceous formations (0-25 m) ...ntaining iron and manganese hydroxides, ...n the lower part a magnesite horizon being ...resent;

2. nontronites and nontronitized serpen-...ites (10-30 m), at the base of the profile ...agnesites are also present;

3. leached serpentinites (10-30 m) with an ...creased content of vermiculite. On the ...undary with the underlying zone the ...rd, lowest, horizon of magnesites occurs;

4. disintegrated serpentinites (up to ...5 m).

The ore bodies of bed-like shape occur ...so in three layers (Fig. 41): (1) in the ...ddle part of the ochreous-siliceous zone, ...here nickel content changes from 0.7 to ...%; (2) in the top part of the nontronite ...ne (Ni from 0.6 to 9.8%); (3) in the lower ...rt of the same zone (Ni from 0.3 to ...%). The total thickness of the ore bodies ...ries from 3 to 25 m. The three-layer struc-...re of the ore deposits is supposed to form ...he three stage process of weathering crust ...ccompanied by uplifting and subsiding of ...oundwater table in Late Triassic-Early ...rassic, in Early Cretaceous and in Late ...ocene-Early Oligocene.

NEW CALEDONIA. About 1 500 silicate nic-...el ore deposits are known on the island. ...bout 1/3 of its territory is occupied by the
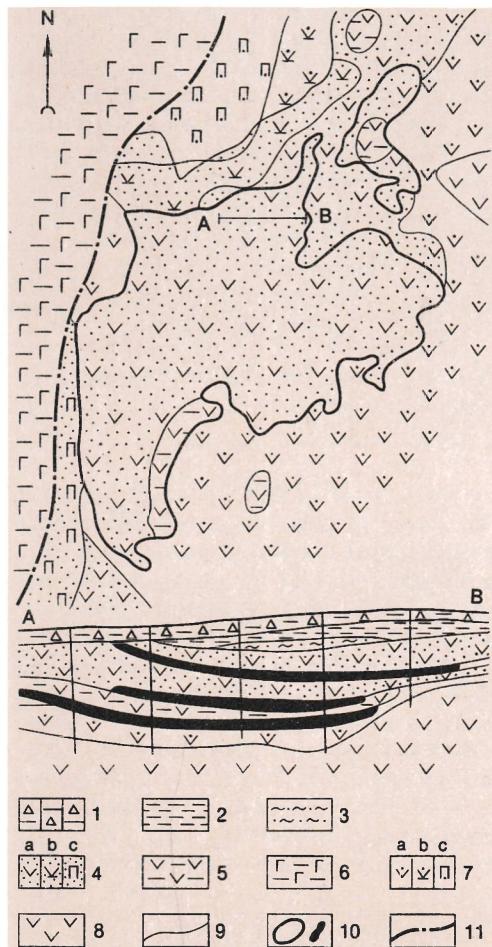
Fig. 41. Scheme of the weathering crust structure in the Sakharinsk deposit of silicate nickel ores. (After F. Sysoyev):
1 – diluvial clays of Quaternary;
2 – variegated clays of Neogene;
3 – clays of Late Oligocene;
4 – ocherous-siliceous formations:
a – after serpentinite;
b – after verlite;
c – after pyroxenite;
5 – nontronitized serpentinites;
6 – montmorillonized and kaolinized gabbro;
7 – leached rocks:
a – serpentinite;
b – verlite;
c – pyroxenite;
8 – apodunite serpentinite affected by weathering;
9 – the boundaries of weathering zones;
10 – ore bodies;
11 – tectonic faults

massifs of serpentinized peridotites of the Neogene age. The massifs are covered by a well-developed lateritic weathering crust (thickness varying from 40 to 50 m) with

In metamorphic processes a concentration of cobalt occurs in pyrites.

The main minerals of the primary cobalt ores are cobalt pentlandite (Fe, Ni, Co)$_9$S$_8$ (up to 3%), linneite Co$_3$S$_4$ (57.96%), cobaltite CoAsS (35-41%), glaucodot (Co. Fe)AsS (33.85%), safflorite (Co, Fe)As$_2$ (28.23%). Arsenides of Co, Ni and Fe form regular paragenetic associations (Fig. 43). In the zone of weathering asbolan is formed m(Co, Ni)O$_2 \cdot$MnO$_2 \cdot n$H$_2$O (up to 19%), whereas in the zone of oxidation of endogenous cobalt ores erythrite is formed Co$_3$As$_3$O$_8 \cdot$8H$_2$O (11-29%).

METALLOGENY

At the early stage of a geosynclinal cycle an insignificant amount of cobalt was tied up with cobalt-bearing pyrites of massive sulfide deposits and with cobalt-bearing magnetites of skarn deposits. At the middle and particularly late stages of this cycle hydrothermal deposits of cobalt ores were formed. During reactivation of platforms cobalt was accumulated in magmatic sulfide deposits together with nickel. During the platform cycle stratiform deposits of cupriferous sandstones containing cobalt were formed, as well as the deposits of weathering crusts over ultrabasic massifs.

In the geologic history of the earth's crust several epochs of cobalt deposit formation are noted, such as Proterozoic (Cobalt, Sudbury in Canada, the deposits in Zambia and Zair, Bu-Azer in Morocco), Caledonian (Khovuaksy in Tuva), Hercynian (Schneeberg in GDR, Jáchymov in Czechoslovakia), Kimmerian (Talnakh in Eastern Siberia, Dashkesan in Transcaucasus) and Alpine (New Caledonia).

TYPES OF COMMERCIAL DEPOSITS

Commercial types of cobalt and cobalt-bearing ore deposits are considered below: (1) magmatic; (2) skarn; (3) plutonogenic hydrothermal; (4) stratiform: (5) weathering crust.
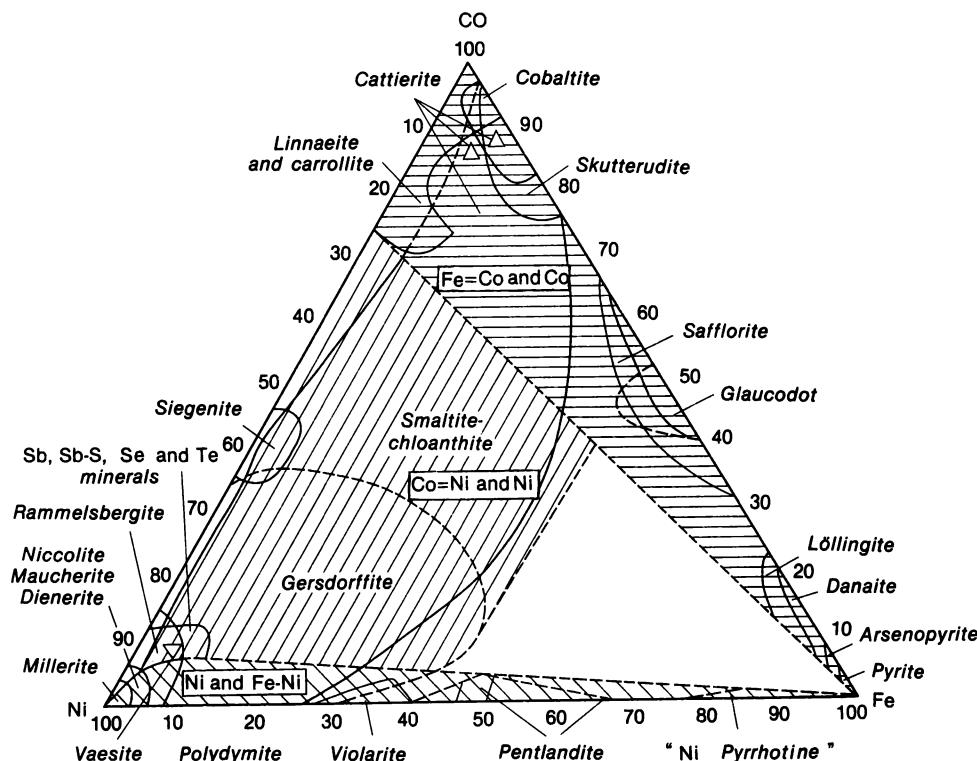
Fig. 43. Basic types of paragenetic hypogenic cobalt and cobalt-bearing minerals. (After G. Krutov)

MAGMATIC DEPOSITS

Magmatic deposits of copper-nickel sulfide ores of liquation origin containing cobalt (such as Talnakh, Oktyabr' in Eastern Siberia, Pechenga in the Kola Peninsula, Sudbury in Canada) are described in the chapter "Deposits of Nickel".

SKARN DEPOSITS

Skarn iron ore deposits containing cobalt-bearing pyrites are represented by lime skarns (Sokolovsk, Sarbai in Kazakhstan), and magnesian skarns (Tayozhnyi in Eastern Siberia). They are described in the chapter "Deposits of Iron".

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal deposits of cobalt are known in the USSR, such as in Tuva (Khovuaksy), in the North-East (Verkhnii Seymchan), in Central Asia (Chalkuyryuk) and Transcaucasus (Dashkesan-Cobalt), and in other countries: GDR (Schneeberg), Czechoslovakia (Jáchymov), Norway (Kongsberg), Morocco (Bu-Azer), Canada (Cobalt), the USA (Blackbird), Australia (Mount Cobalt). They are related to granitoid intrusions. The enclosing rocks are represented by sedimentary and metamorphic formations, skarns or serpentinites. Ore bodies have the form of veins and stockworks. The ores are mostly complex (Co-Ni, Co-Ni-Ag, Co-Ni-Bi-Ag-U, and Co-Ni-Cu-Pb-Zn). Pre-ore alterations of the rocks consisted of tourmalinization, biotitization, sometimes skarnification or sericitization. The alterations surrounding ore bodies consisted of silicification, epidotization, chloritization and carbonatization. Formation of minerals occurred in several stages, three of them being principal: (1) arsenopyrite-cobaltite-quartzite; (2) smaltite-chloantite; and (3) sulphide-carbonate.

Among plutonogenic hydrothermal deposits of cobalt one can distinguish the following ore formations: (1) smaltite-chloantite-nickeline-argentite (Khovuaksy in the USSR, Cobalt in Canada); (2) arsenopyrite-glaucodot-cabaltite (Dashkesan-Cobalt in the USSR, Bu-Azer in Morocco); (3) five metals formation Co-Ni-Bi-Ag-U (Eldorado in Canada).

The Deposits of Smaltite-chloantite-nickeline-argentite Formation

KHOVUAKSY. The deposit is located in Tuva. The area of the deposit is composed of Cambrian volcanics, Silurian sedimentary strata with horizons of skarnified limestones (thickness up to 120 m) and Lower Devonian volcanogenic and sedimentary rocks that are overlain by unconformable Givetian sedimentary deposits. Subvolcanic rocks of basic, intermediate and alkaline composition are developed. Intrusive formations are represented by the massifs of Caledonian granitoids (460-480 mln years) pre-skarn and post-skarn (but pre-ore) dikes of diabases and diabase porphyries, as well as by the stocks of Early Hercynian granites. Silurian and Lower Devonian rocks form an anticline complicated by faults. Mineralization is related to submeridional large-amplitude fault with gentle or steep feather fractures that cut the skarns (Fig. 44).

Fig. 44. Scheme of the geological structure of the Khovuaksy ore field. (After A. Bogomol): ▶

1 – Paleogene-Neogene and Quaternary sediments;
2 – Givetian sedimentary rocks;
3 – Lower Devonian sedimentary-volcanogenic rocks;
4-7 – Silurian rocks:
    4 – conglomerates, sandstones, aleurolites (member a);
    5 – interlayered skarns and aleurolites (member b);
    6 – skarns (member c);
    7 – interlayered aleurolites and sandstones (member d);
    8 – volcanogenic rocks of Lower Cambrian;
9 – granites;
10 – trachitic porhyry dikes;
11 – subvolcanic sheets of diabases, gabbro-diabases, diabase porphyrites;
12 – subvolcanic sheets of andesite porphyrites;
13 – diabase dikes;
14 – quartz porphyry dikes;
15 – faults:
    a – of the first order (1 – South-Western fault;
    2 – Northern thrust;
    3 – North-Western (Zherlov) fault;
    4 – Western fault;
    5 – Eastern fault);
    b – faults of various orders;
16 – ore veins;
17 – sectors of the Eastern block of the ore field:
    I – Southern;
    II – Northern;
    III – Middle;
    IV – Intermediate
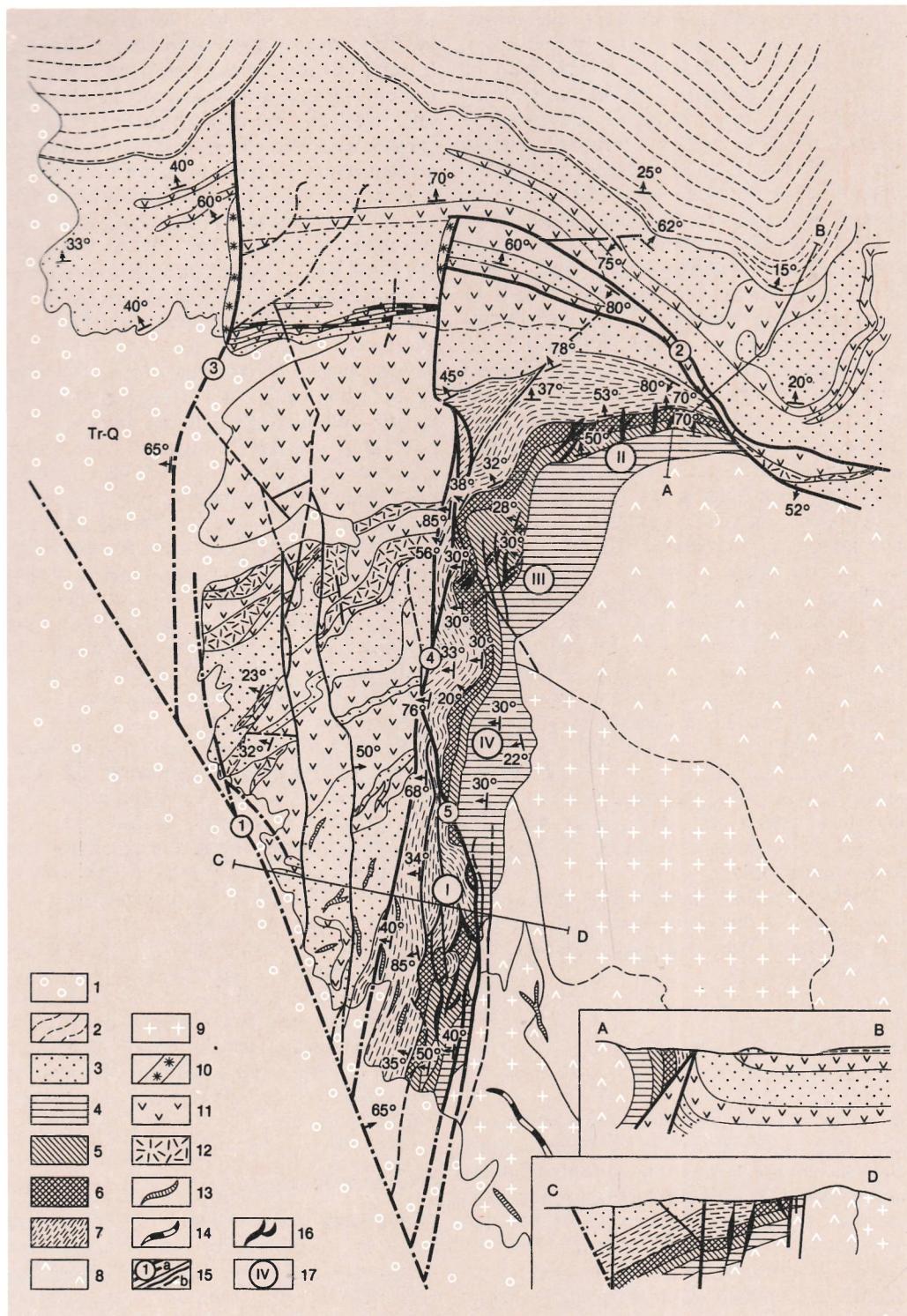
Ore bodies are represented by veins which often crosscut the skarns. Ore shoots occur in the places of junction and branching of fissures or in the places of change in their setting. The ores have a nickel-cobalt composition. The main ore-forming minerals are: nickeline, rammerlsbergite, smaltite, chloantite, skutterudite and safflorite; main gangue minerals are calcite and dolomite; subordinate ore minerals are: grey ore, chalcopyrite, sphalerite, galena, native bismuth, native silver and argentite, as well as gangue siderite, chlorite, quartz and barite.

Among minerals of the oxidation zone one finds erythrite and annabergite. The structures of the ores can be banded, brecciform, streaky and disseminated. Textures can be crystalline, radial, colloform and zonal. Pre-ore alterations of the enclosing rocks consist of skarnification of limestones, whereas alteration developed around ores is manifested in carbonatization. In the early stage of mineralization safflorite-smaltite and smaltite-rammerlsbergite-nickeline associations with calcite, dolomite and siderite were formed. In the later stage of the mineralization sulfides with calcite, quartz and barite were segregated. Horizontal zonality is demonstrated by the fact that the central parts of the ore bodies are formed of arsenides of Co, Ni and Fe in association with calcite and dolomite, while peripheral parts of the ore bodies are composed, besides carbonates, of chlorite and copper sulfide.

The Khovuaksy deposit was formed in the final stages of the Caledonian cycle, at the end of the Lower and beginning of the Middle Devonian.

The Deposits of Arsenopyrite-glaucodot-cobaltite Formation

BU-AZER. The deposit is located in Morocco. The area is composed of Archean orthogneisses and overlying unconformable metamorphosed volcanogenic-sedimentary formations of Lower Proterozoic that are overlain by a platform sedimentary cover of Upper Proterozoic-Lower Paleozoic. The deposit is confined to a deep-seated fault which is marked by serpentinites, spilites and quartz diorites. Mineralization is localized in the brecciated zones that are located along the contact between a dome-shaped projection of serpentinites and overlying rhyolites. The ore enclosing rock is represented by a quartz-carbonate veined mass which is confined to the contact. It makes up a complicated deposit up to 30 m-thickness that goes to the depth of 400 m (Fig. 45). Ore bodies have the shape of lenses, veins and columnar bodies traceable along the dip down to 250-300 m with the thickness from 10-15 to 30 m.

The main ore-forming minerals are: skutterudite, safflorite, lollingite, rammelsbergite and niccolite; gangue minerals are: dolomite, calcite, antigorite, chrysotile-asbestos, serpophite; subordinate minerals are: arsenopyrite, cobaltite, pyrite, gersdorffite, chalcopyrite, molybdenite, bornite, magnetite, hematite, chrome-spinellides, brannerite, native silver, native gold, realgar and orpiment, as well as talc, chlorite and quartz. Erythrite and annabergite are developed in the oxidation zone (down to 30-50 m). The structure of the ores can be massive, brecciform, streaky and disseminated.

Mineralization was formed in three main stages: (1) brannerite-molybdenite; (2) skutterudite-nickeline; (3) chalcopyrite-bornite. The primary horizontal zonality is very explicit and manifested in the domination of cobalt and iron-cobalt ores in the central zone, cobalt-nickel in the intermediate, and nickel ores in the peripheral zone.

The age of the primary ores in the Bu-Azer deposit is Late Proterozoic. Subsequent transformation of the ores took place in the Hercynian and Alpine epochs. The ores were formed at the depth of around 500 m. During the process both Co and Ni were taken from serpentinites by hydrothermal solutions.

STRATIFORM DEPOSITS

Commercial concentrations of cobalt are found in stratiform deposits of cupriferous sandstones in Zambia and Zaire which are described in the chapter "Deposits of Copper".
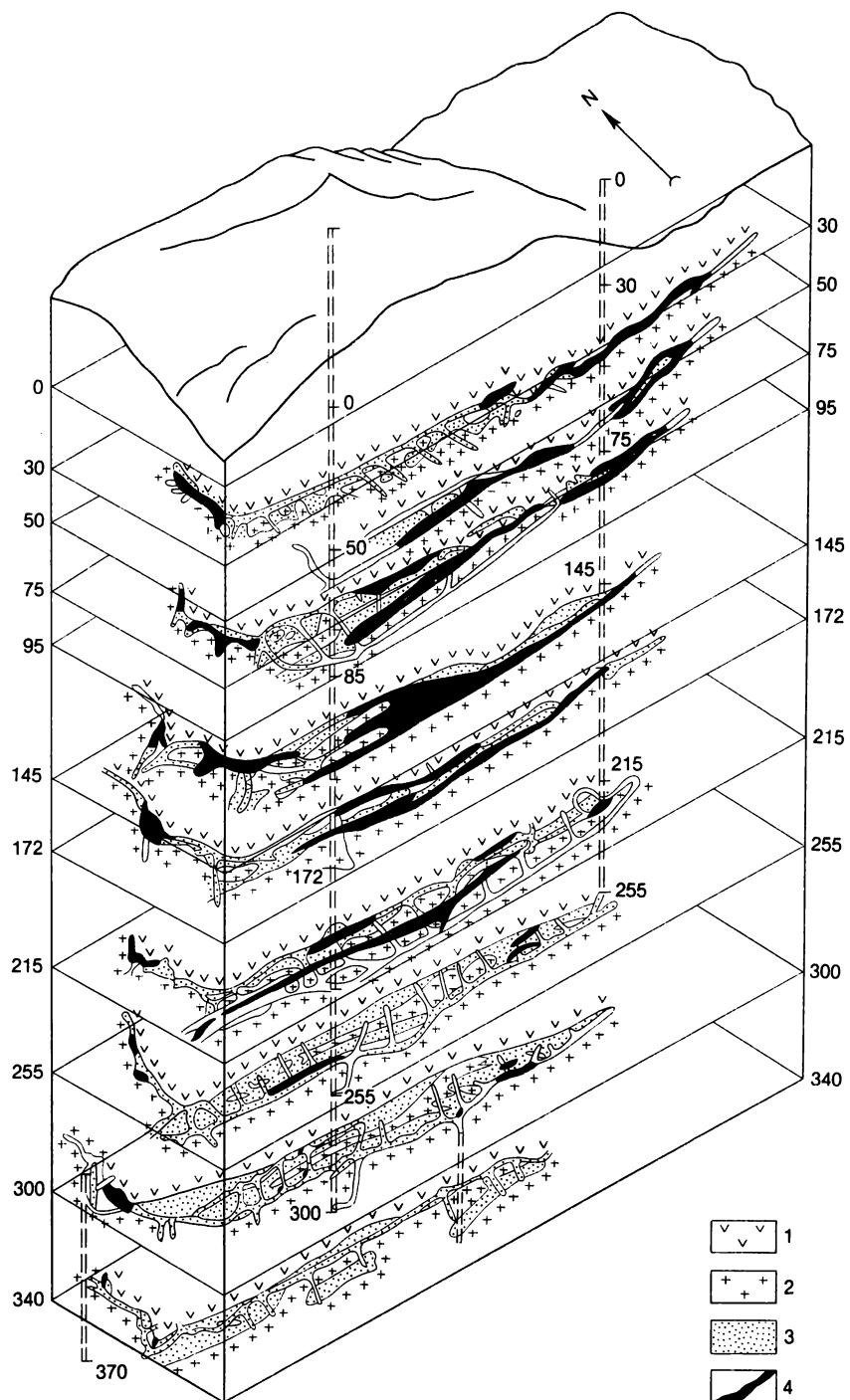
Fig. 45. Block-diagram of the Bu-Azer deposit. (After G. Krutov):

1 — serpentinites;
2 — quartz diorites;
3 — quartz-carbonate vein mass;
4 — ore

DEPOSITS OF WEATHERING

Nickel-bearing weathering crusts contain cobalt ores that are represented by asbolan. These deposits are described in the chapter "Deposits of Nickel".

10 COPPER DEPOSITS

Copper is known from the Bronze Age, which spanned the period from 4000 to 1000 B.C. Utilization of copper is based on its high electric conductivity, chemical stability, plasticity and its capacity to form alloys with many metals, such as tin (bronze), zinc (brass), nickel (cupronickel), etc. Copper is used in many different branches of industry, such as electrical engineering and communication (50%), machine-building (25%), construction, food and chemical production (25%). Copper is obtained from copper, copper-molybdenum, copper-nickel and polymetallic ores. Plants produce raw copper (99%), refined (99.6%) and electrolytic copper (99.95%). The price for refined copper in 1975 was 1240 US dollars per ton. In 1975 capitalist and developing countries produced 5800 thousand tons of copper. The prospected copper reserves ran to 345 mln tons, total – to 465 mln tons. Unique deposits have the reserves of over 5 mln tons of copper (El-Teniente, Chuquicamata in Chile, and others). Very large deposits have 5-1 mln tons, medium-size – 1-0.2 mln tons and small deposits have reserves of less than 0.2 mln tons of copper. High-grade ores contain 3-2.5% of copper, regular ores contain 2.5-1%, and low-grade ores less than 0.5% of copper.

GEOCHEMISTRY AND MINERALOGY

Copper is represented in nature by two isotopes, i.e. ^{63}Cu (69.09%) and ^{65}Cu (30.91%). The crustal abundance (clarke) of copper is $4.7 \cdot 10^{-7}\%$, its abundance being somewhat higher for basic $(1 \cdot 10^{-2})$ than for acidic rocks $(1 \cdot 10^{-3})$. The clarke of concentration for copper is 200. Copper is classified as polymagmatogenic and is related both to basaltophile and granitophile elements. In case of basaltic magmatism it tends to concentrate both at plutonic stage, forming liquation and skarn deposits, and at volcanic stage when postvolcanic massive sulfide deposits are formed. In relation to granitic magmatism postmagmatic deposits of copper are formed, the latter is transported by hydrothermal solutions, most probably in the form of thiosulphate and chloride complex compounds.

Under exogenous conditions copper concentrates, first of all as a result of hypergenic alterations of sulfide ores which leads to formation of oxidation zones and secondary sulfide enrichment. Copper also concentrates in terrigenic sediments of the lagoon-deltaic and coastal parts of marine basins.

Transportation of copper in this case is also possible in the form of complex compounds. For example, it forms a phosphate-carbonate complex which, according to V. Shcherbina, is kept in solutions even at relatively high values of pH = 10.5.

Over 170 minerals of copper are known, however, commercial importance is attributed to no more than 17. They include: native copper Cu (92%), chalcopyrite $CuFeS_2$ (34.6%), bornite Cu_5FeS_4 (63.3%), cubanite $CuFe_2S_3$ (22-24%), chalcosine Cu_2S (79.9%), covellite CuS (66.5%), tennantite $3Cu_2S \cdot As_2S_3$ (57.5%), tetrahedrite $3Cu_2S \cdot Sb_2S_3$ (52.3%), enargite Cu_3AsS_4, cuprite Cu_2O (88.8%), tenorite CuO (79.9%), malachite $CuCO_3 \cdot Cu(OH)_2$ (57.4%), azurite $2CuCO_3 \cdot Cu(OH)_2$ (55.3%), chalcanthite $CuSO_4 \cdot Cu(OH)_2$ (31.8%), brochantite $CuSO_4 \cdot 3Cu(OH)_2$ (56.2%), atacamite $CuCl_2 \cdot 3Cu(OH)_2$ (59.5%), and chrysocolla $CuSiO_3 \cdot nH_2O$ (36.0%). Copper sulfides (chalcopyrite, chalcosine, bornite) appear to be the most important minerals in the copper ores, secondary value is attributed to sulphosalts (grey copper ores) and sulphoarsenides (enargite). Oxides, carbonates and silicates of copper are less important.

The associations of the main ore-forming minerals of copper are shown in the system Cu-Fe-S-O (Fig. 46).
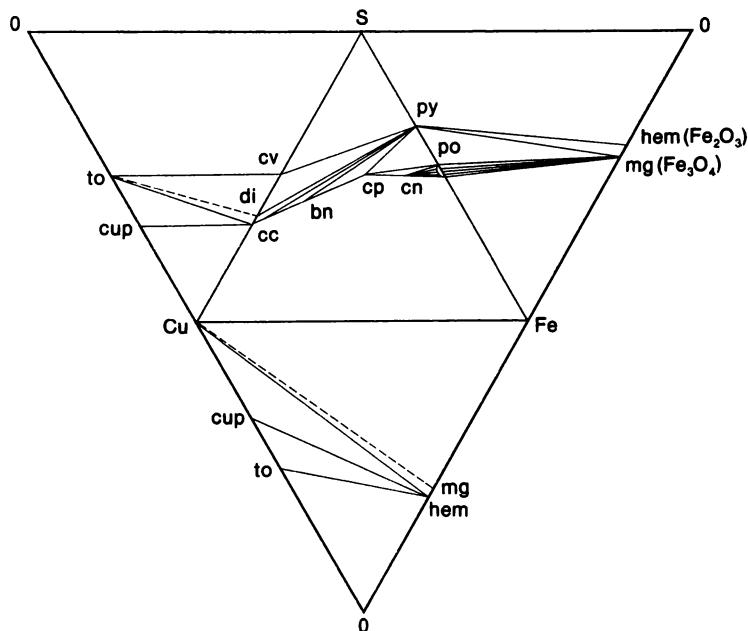
Fig. 46. Assemblage of copper minerals in the Cu-Fe-S-O system:

to – tenorite;	cc – chalcocite;	py – pyrite;
cup – cuprite;	bn – bornite;	po – pyrrhotite;
cv – covellite;	cp – chalcopyrite;	hem – hematite;
di – digenite;	cn – cubanite;	mg – magnetite

METALLOGENY

At the early stage of geosynclinal development, in relation to basaltoid volcanism of eugeosynclines, large-size magmatic massive sulfide deposits of copper were formed. At the termination of this stage, in relation to plagiogranites, skarn ore deposits of copper and iron and also early deposits of porphyry copper ores were formed. At the middle stage of a geosynclinal cycle, no significant copper deposits originated. At the late stage the main proportion of hydrothermal deposits was formed. The leading place among them is attributed to late porphyry copper deposits related to moderately silicic intrusions. Approximately at this stage large-size stratiform deposits of cupriferous sandstones were formed in the sediments of molasse formation which composed the superimposed troughs. Cupriferous sandstones and cupriferous shales accumulated during the platform cycle in terrigenous sediments that formed the troughs in the platform sedimentary cover. During the reactivation

stage of the platform cycle magmatic copper-nickel sulfide deposits were formed in relation to the stratified basaltoid complexes.

Large copper deposits such as stratiform cupriferous sandstones in the African and Siberian platforms, magmatic copper-nickel ores in the Canadian, East-European and African platforms, volcanogenic hydrothermal native copper deposits in the Canadian platform were formed during the Proterozoic magmatic epoch. Magmatic copper massive sulfide deposits in the folded areas of the Urals, Northern Caucasus, Appalachia, Pyrenees and some other regions were the most important during the Caledonian and especially Hercynian epochs. Plutonogenic hydrothermal deposits of porphyry copper ores in Kazakhstan and Central Asia, as well as stratiform deposits in Kazakhstan, Poland, GDR, were also formed at this stage. During the Kimmerian metallogenic epoch large copper-nickel deposits in the Siberian and African platforms emerged, as well as porphyry

copper and massive sulfide deposits in the folded provinces of Transcaucasus and Balkan. During the Alpine epoch very large hydrothermal deposits of porphyry copper ores were formed, alongside with massive sulfide deposits within the circum Pacific belt, and partially in the Mediterranean belt.

TYPES OF COMMERCIAL DEPOSITS

Among the commercial deposits of copper one can distinguish: (1) magmatic; (2) carbonatite; (3) skarn; (4) plutonogenic hydrothermal; (5) volcanogenic hydrothermal; (6) massive sulfide; (7) stratiform.

MAGMATIC DEPOSITS

Liquation deposits of copper-nickel sulfide ores related to intrusions of ultrabasic-basic rocks have a dominating importance in this group of deposits. The ores are complex and cobalt, gold platinoids and trace elements are extracted from them besides copper (content above 1-2%) and nickel. Copper accumulates at the end of the ore formation process, when chalcopyrite and bornite are segregated. Exocontact zones of intrusions are enriched by it. Copper-nickel deposits are described in the chapter "Deposits of Nickel".

CARBONATITE DEPOSITS

One such deposit is known in the South African Republic (Palabor). Admixtures of copper minerals have been found in some carbonatites in Siberia and the Kola peninsula.

PALABOR. The deposit is confined to a massif of ultrabasic alkaline rocks that intruded Archean granites. It has a pipe-shaped body (0.5-0.7 km-thickness), the core being composed of carbonatites, while at marginal parts it is made of magnetite-apatite ores. Zones of streaky-disseminated copper ores in the carbonatites are traced down to 900 m. The main minerals are bornite, that was formed during the first stage of mineral formation, and chalcopyrite that was segregated in the second stage. The subordinate minerals are chalcosine, valleriite, cubanite

and magnetite. The deposit is complex and contains copper (average content 0.68%), iron and phosphate ore. Copper reserves in the deposit are estimated as 1.5 mln tons.

SKARN DEPOSITS

In the USSR skarn deposits of copper are known in Kazakhstan (Sayak I), in the Urals (Tur'ya group), in Western Siberia (Yulia), and in other countries: in the USA (Clifton, Bisbee), Mexico (Dolores), etc. They are represented by lime skarns of garnet-pyroxene composition, with sulfides that were superimposed during aposkarn stage. Sulfides form in enclosing skarns lenses, pockets and pillar-like bodies. The main ore minerals are chalcopyrite, pyrrhotite, pyrite and magnetite. Gangue minerals include, besides garnet and pyroxene, epidote, chlorite, quartz and carbonates. Copper content is high but irregularly distributed (10-1%, in average being 1.5-3%). Chalcopyrite crystallization relates to several stages, i.e. during the initial one together with magnetite, in the later stage alongside with other sulfides, and sometimes during the final stage together with prevailing sphalerite and galenite.

The skarn copper deposits are of different ages, namely, of Paleozoic in the USSR, and of Mesozoic and Cenozoic in other countries. They are related to moderately silicic sodium granitoids, which mainly belong to the early stage of a geosynclinal cycle. The formation depth of these deposits is no less than 1-1.5 km. The temperature range of formation of copper sulfide ores varies from 500 to 200 °C.

SAYAK I. The deposit is located in Kazakhstan. The area consists of carboniferous volcanogenic-sedimentary strata with interlayers of limestone having the thickness up to 150-200 m. They form an asymmetric anticline whose eastern wing is intruded by granitoids and dikes of Carboniferous age. A succession of faults and thrusts complicates the folded structure of the area (Fig. 47). The contact plane of the intrusive has a steep dipping westward, in places eastward. Garnet-pyroxene skarns are developed after limestones in the exocontact of the intrusive forming a zone with the
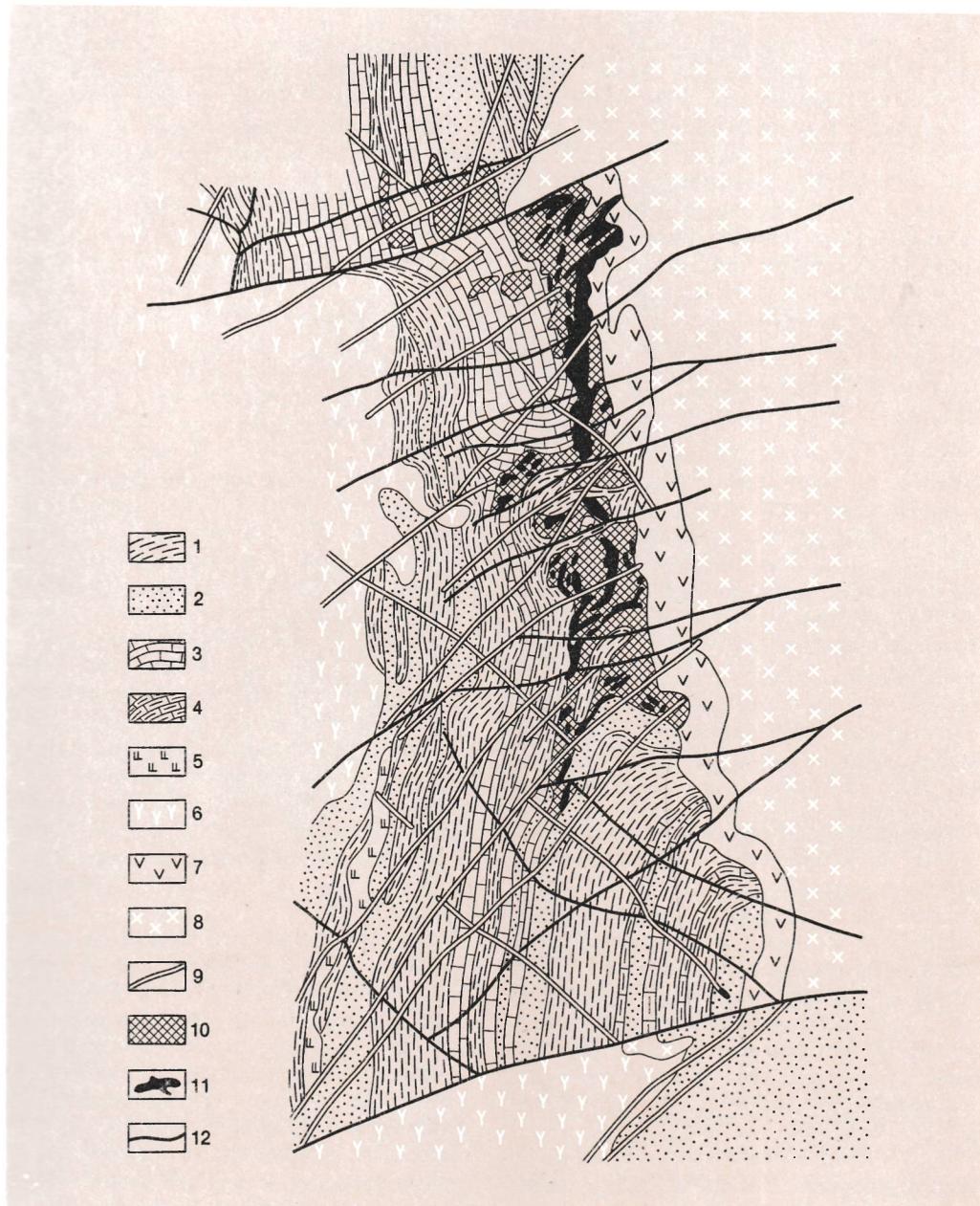
Fig. 47. Schematic geological map of the Sayak I deposit. (After G. Burdukov and L. Tarnovsky):

1-4-lower-middle-carboniferous sediments:
1-tuff-aleurolites;
2-sandstones;
3-limestones;
4-calcareous tuff-aleurolites;
5-subvolcanic diorite-porphyry bodies;
6-Permian(?) effusives of intermediate and basic composition;

7-8-upper carboniferous intrusive rocks:
7-diorites;
8-granodiorites and quartz diorites;
9-dikes of diorite and diabase porphyrites, granodiorite-porphyries;
10-skarns;
11-ore bodies;
12-tectonic faults

length of 3 km and the width 0.5-1 km.

Two types of ore bodies can be distinguished: lenticular bodies in skarns (thickness up to 10-15 m), and zones of streaky-disseminated ores in granitoids. The main minerals of the primary ores are chalcopyrite, magnetite, bornite, pyrrhotite, arsenopyrite and cobaltite. The main gangue minerals are represented by garnet, pyroxene, scapolite, actinolite, epidote, quartz and chlorite; the subordinate minerals are pyrite, molybdenite, sphalerite, and galenite. Besides copper, the ores contain Mo, Au, Hg, Co, Bi, Se, and Te. An east-west succession of the zones of metasomatites from the contact of granodiorites with enclosing rocks has been established in the following order: (1) pyroxene-garnet skarns with magnetite, partially bornite and chalcopyrite and accompanying pyroxene-feldspar rocks (the width of the zone 10-180 m); (2) garnet skarns with molybdenite, bornite and chalcopyrite (100-200 m); (3) epidote-actinolite-chlorite rocks with arsenopyrite-cobaltite mineralization (5-50 m).

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal deposits of copper are associated with hypabyssal porphyric intrusions of a moderately silicic composition, more seldom with granitoids. Ore-bearing intrusions are the members of volcano-plutonic formations and are mainly related to the later stage of a geosynclinal cycle, or to reactivation of ancient platforms. Among the plutonic hydrothermal deposits, porphyry copper and vein deposits are distinguished.

Porphyry-copper Deposits

Porphyry-copper deposits are large accumulations of low-grade copper or molybdenum-copper streaky-disseminated ores of stockwork type located in porphyric intrusions. Such deposits are known in the USSR in Kazakhstan (Kounrad), Central Asia (Kalmakyr), and Transcaucasus (Kadzharan), and in other countries: in Yugoslavia (Majdanpek), Bulgaria (Medet, Aṣarel), Iran (Sar Chesmeh), Mongolia

(Erdentuin), Chile (El Teniente), Peru (Toquepala), Panama (Cerro Colorado), the USA (Bingham, Morenci, San Manuel), Canada (Valley Copper, Endako), etc.

Four groups of such deposits in terms of the copper-molybdenum ratio, as well as other properties, can be distinguished, according to A. Krivtsov (1977); (1) molybdenum-porphyry with a subordinate importance of Cu, these deposits being related to granite-porphyry of granite complexes which belong to potassium series (Climax, USA; Kadzharan, USSR); (2) porphyry-copper-molybdenum deposits associated with quartz-monzonite porphyries of potassium-sodium granitoids (Chuquicamata, Chile); (3) porphyry-copper deposits with an insignificant admixture of molybdenum related to granodiorite-porphyries of granodiorite complexes (Kounrad, USSR; El Teniente, Chile); (4) porphyry copper with clarke contents of molybdenum associated with diorite porphyries of gabbro-diorite complexes of sodium series (Salavat in the Urals). The deposits of the first three groups were formed during the final stage of a geosynclinal cycle in the provinces having a continental crust and are related to a "monzonite" type. The deposits of the fourth group were formed during the early stage of a geosynclinal cycle in the areas with an oceanic crust and are related to a "diorite" type (V. Hollister, 1975).

Stocks and dikes of moderately silicic intrusions located at intersections of faults, flexures, anticlines and volcanic domes play a leading role in the structure of these deposits. Pipe-like bodies composed of explosive breccia are often encountered.

The ore bodies are represented by stockworks of an oval or annular shape in a horizontal section, and of a cylindrical or conical shape in a vertical section. Their shape is often determined by the structure of the apical zone of intrusive stocks. The stockworks have the length of 2-3 km and the width of 0.7-1.5 km. In case of a concentric shape the dimensions of the stockworks vary from a few hundreds of metres to one km crosswise. A vertical extension of mineralization can be 300-500 m and more. The ores are represented by
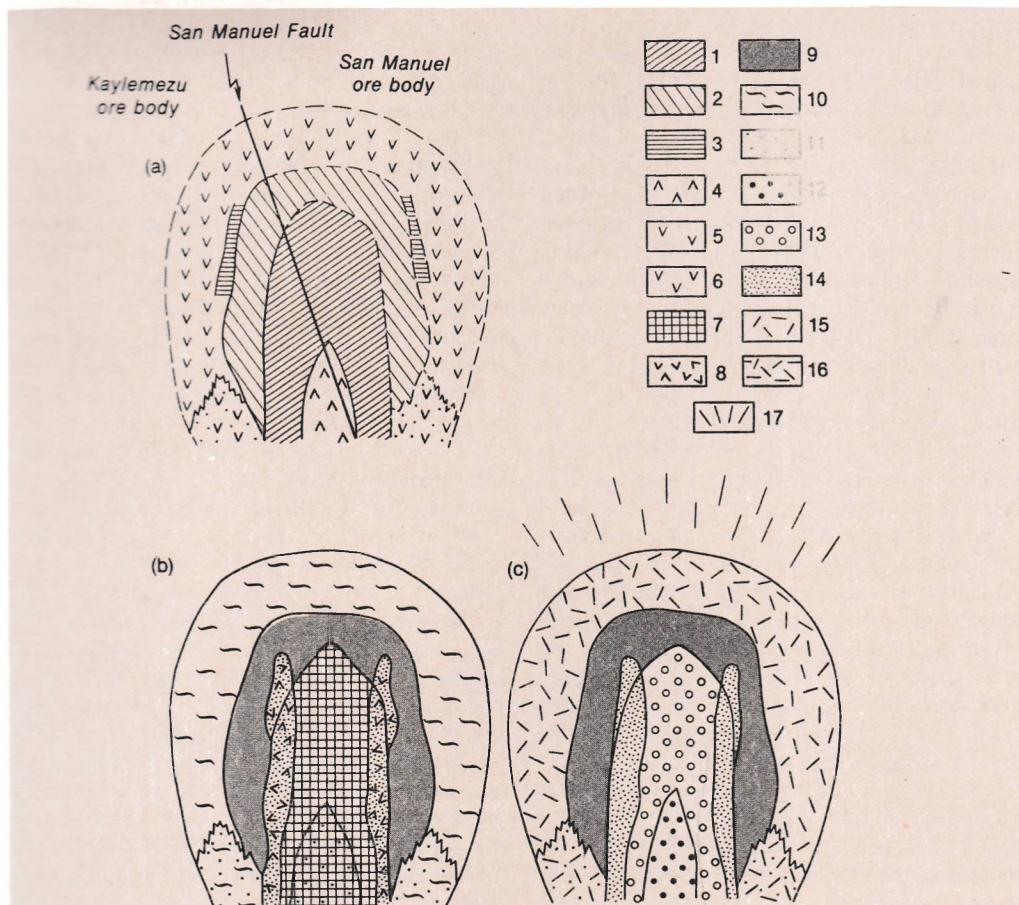
Fig. 48. Scheme of the metasomatic and ore zonality of porphyry-copper deposits on the example of the San-Manuel deposit in the USA. (After G. Lowell and J. Gilbert):

a – metasomatite zonality;
b – ore mineralization distribution;
c – distribution of disseminated and stringer mineralization.
1 – metasomatites:
1 – orthoclasites;
2 – felsites;
3 – argillites;
4 – propylites;
4 – quartz-sericite-chlorite-orthoclasite;
5 – chlorite-sericite-epidote;
6 – chlorite-epidote;
7-11 – ore distribution:

7 – the core of low-grade ores;
8 – the ore body (pyrite 1%, chalcopyrite 1-3%);
9 – pyrite shell (pyrite 10%, chalcopyrite 0.1-03%);
10 – peripheral zone of polymetallic mineralization;
11 – magnetite development zones;
12-16 – ores:
12 – disseminated;
13 – disseminated and micro-stringer;
14 – disseminated ores dominating over stringer;
15 – stringer ores and mineralization, dominating over disseminated;
16 – disseminated mineralization;
17 – outer zone of large veins

thin network of quartz and quartz-feldspar veinlets (with the thickness in the range of a few millimetres-centimetres) containing sulphides which also form impregnations and pockets. The main minerals of the primary ores are chalcopyrite and pyrite. The gangue minerals are quartz and sericite. The subordinate minerals are represented by molybdenite, bornite, hypogenic chalcosine, enargite, grey copper ore, galena, sphalerite, magnetite and hematite and also by feldspars, calcite and anhydrite. Average copper content in the primary ores is 0.2-0.7%, while in the zone of secondary enrichment it increases up to 1-1.5%. Mo (0.005-1.05%), Se, Te and Re are also

extracted as by-products. The structures of the ores can be streaky-disseminated, rarely brecciform. The textures could be hypidiomorphic-granular, porphyry, corrosion, etc.

The veinlets in the ores were formed in three stages. The first is the premineral stage, when quartz-feldspar veinlets with very low-grade sulfide mineralization and with magnetite were formed. The second is the ore stage when, first, quartz veinlets with molybdenite, chalcopyrite, pyrite and then quartz and quartz-carbonate veinlets with grey copper ore, sphalerite, galena, gold, silver, and other minerals were formed. At the final post-ore stage chalcedony-calcite veinlets with anhydrite, fluorite, barite and hematite appeared.

Ore-bearing rocks, such as intrusive porphyries and granitoids, and partially volcanics and sedimentary rocks, were subjected to intensive hydrothermal alterations. Concentric zonality in ore mineralization is observed (A. Krivtsov, I. Yudin, 1976; V. Popov, 1977; E. Sillitoe, 1973). Three zones can be delineated: (1) the internal, with disseminated copper ores (pyrite, chalcopyrite, bornite, molybdenite, magnetite) in orthoclasites, and partially in quartz-sericite metasomatites; (2) the intermediate, with streaky copper ores and profuse pyritization in quartz-sericite and argillized metasomatites; (3) the outer, with vein polymetallic mineralization in propylites (Fig. 48). The primary vertical zonality is manifested in an enrichment of the ores in bornite and chalcosite upwards, and in an increase of the role of ore streaks in the same direction.

In terms of commercial evaluation of porphyry-copper deposits, a great importance has the zone of oxidized ores, which manifests a secondary zonality. The scheme of this vertical secondary zonality is represented in a sequence of the following zones (downwards): (1) oxidation (up to 100-200 m, normally 10-30 m), composed of malachite, azurite, cuprite, tenorite, chrysocolla, native copper; (2) leaching zone (thickness 20-25 m); (3) secondary sulfide enrichment zone (thickness from a few tens to 200-300 m), composed of chalcosite, partially covellite; copper concentration in

this zone increases 1.5-2.5-fold in comparison with that in primary ores, which are substituted by this zone at the depth of a few hundred metres.

The depth of formation of porphyry-copper deposits ranges from a few hundreds of metres to 2.5-2 km. The temperature range for the mineral formation is from 700-600 °C at the initial stages to 100 °C and lower at the final stages of mineralization as estimated in the studies of fluid inclusions; copper sulfides are segregated in the temperature range of 350-250 °C. The fluid inclusions at the early stages of mineralization contain concentrated solutions of chloride composition, while water solutions at the later stages are enriched with carbonic acid. The sulphur isotope study of sulfides has shown that $\delta^{34}S$ is close to zero, but in different deposits it may vary from $+3.1$ to -2.7%.

KOUNRAD. This deposit is located in the territory of Kazakhstan. The area is made of Lower Carboniferous volcanics of liparite composition that make up a volcanic dome structure. The volcanic chimney is intruded by a stock of granodiorite-porphyries which belong to a supplementary phase of the Middle Carboniferous granitoid complex. The ore body is confined to the apical zone of the stock and together with the enclosing metasomatites follows its contour (Fig. 49). The ore body looks like a stockwork whose setting is determined by a network of conical-annular fissures. Altered granodiorite-porphyries contain sulfide impregnations and are cut by multiple quartz and quartz-sulfide veinlets that have the thickness of a few centimetres, and the length from tens of centimetres to a few metres. The main ore minerals are pyrite, chalcopyrite, molybdenite, enargite and grey copper ore. Quartz is the main gangue mineral. Subordinate minerals are sphalerite, bornite, galena and magnetite, as well as kaolinite, andalusite, sericite, tourmaline, alunite, pyrophyllite, epidote, diaspore and chlorite. Besides copper, the ores contain Mo, As, Pb, Zn and trace elements. The structures of the ores can be disseminated, streaky-disseminated, brecciform. The textures can be cement-like, replacement, of common boundaries and network-lattice.
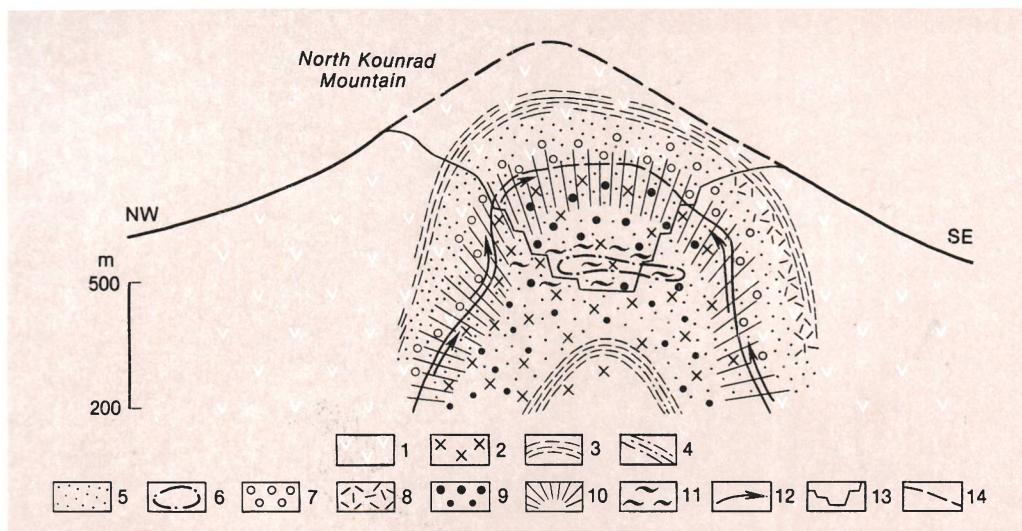
Fig. 49. Schematic geological section of the Kounrad deposit. (After I. Yudin):

1 – liparite porphyries;
2 – granodiorite-porphyries;
3-8 – metasomatites:
   3 – propylites and propylitized rocks;
   4 – argillitized;
   5 – quartz-sericite;
   6 – quartz-kaolinite;
   7 – quartz-andalusite;
   8 – diaspore-pyrophyllite;
9-11 – zones of dominating primary mineralization:
   9 – copper;

10 – molybdenum-arsenic;
11 – galenite-sphalerite;
12 – the main direction of hydrothermal solutions migration;
13 – recent contour of the surface of the deposit and the open pit;
14 – supposed contour of the granodiorite-porphyry stock and the Northern Kounrad Mountain before the ore body erosion started. Vertical scale of the section is larger than horizontal

The paragenetic associations (according to prevailing minerals) segregated in the following sequence: pyrite, molybdenite, enargite and galena-sphalerite. According to studies of fluid inclusions in gangue minerals (quartz, barite, sericite) by homogenization and decrepitation techniques the pre-ore stage (secondary quartzites) developed in the temperature range from 500 to 300 °C, the ore stages had the temperature range from 460 to 110 °C, whereas the post-ore stage (barren veinlets) occurred at the temperatures from 180 to 70 °C (E. Yudin, 1969).

The enclosing rocks were subjected to metasomatic alterations whose intensity decreased upward and downward with the distance from the contact between granodiorite-porphyries and extrusive liparite-porphyries. The zonality pattern at both sides of the contact is as follows: secondary quartzites are developed after granodiorite porphyries, being substituted with depth by argillizites and propylites. Secondary quartzites are also developed after

liparite-porphyries being replaced by propylites at the maximum distance from the contact. The ores are confined to sericite and kaolinite varieties of the secondary quartzites developed after granodiorite-porphyries. The primary ore zonality is concentric one: the richest copper mineralization is confined to the central and upper portions of the ore body, whereas molybdenum-arsenic mineralization occurs in the peripheral zone of the stockwork. The secondary zonality manifests itself in a vertical succession (downward) of the following zones: (1) oxidation zone (a few tens of metres); (2) leaching zone (of the thickness from 0 to 80 m); (3) the zone of secondary sulfide enrichment, which at the depth of 250-300 m is substituted by the primary ores that have been intersected by boreholes down to the depth of 600-650 m. The total vertical range of mineralization is estimated to be from 800 to 1 000 m.

CHUQUICAMATA. The deposit is located in Chile. Starting from 1915, ten million tons
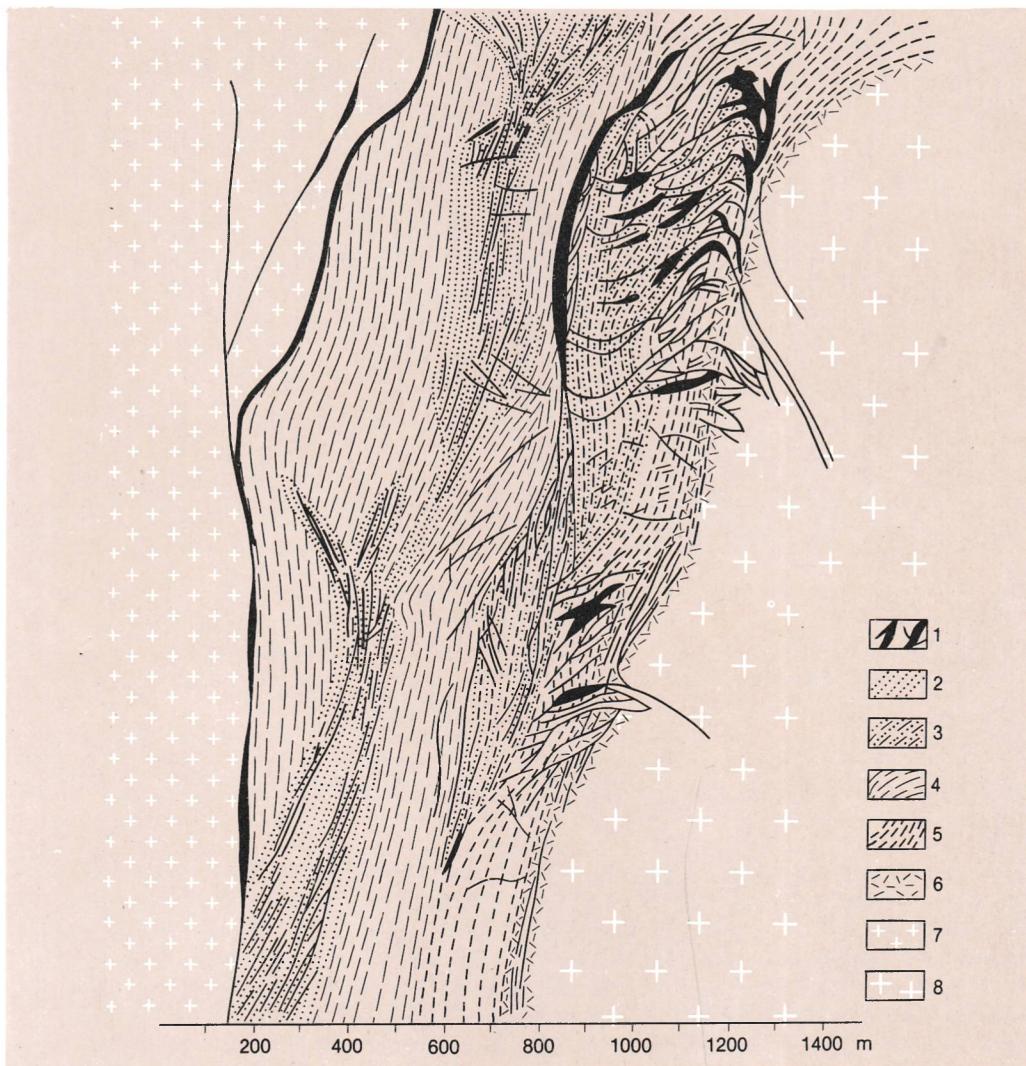
Fig. 50. Scheme of the geological structure of the Chuquicamata porphyry-copper deposit. (After V. Lopez and V. Perri):

1 – ore veins and stringers (stockwork zone);
2-6 – altered Paleogene monzonite porphyries:
  2 – silicified;
  3 – sericitized and slightly silicified;
  4 – extensively sericitized;
5 – albitized and sericitized;
6 – chloritized and albitized;
7 – Paleogene granodiorites (Fortune);
8 – Jurassic granodiorites (Helen)

of copper in total has been produced. The remaining copper reserves are estimated as 25 mln tons with the average content 1.25%. The remaining reserves of molybdenum are estimated as 120 thousand tons with the average content 0.006% (V. Pervago, 1975). The deposit is confined to an Oligocene intrusive of monzonite-porphyries (28 m. y.). In the east the intrusive breaks through Jurassic granodiorites (150 m. y.), while on the west side it borders Paleogene granodiorites (30-60 m. y.) along the fault. The ore body is represented by a stockwork which extends from north to south over 3 km with the width being 0.8 km. The stockwork is formed by a dense network of mineralized veinlets and branching veins (Fig. 50). The main minerals of the primary

are pyrite, enargite and chalcopyrite. The subordinate minerals are bornite, sphalerite. galena and molybdenite. The enclosing rocks are extensively altered by hydrothermal processes, being sericitized, and partially silicified and chloritized.

There is a horizontal zonality trend related to the above mentioned fault. This zonality is manifested by the three following zones: the Western zone containing copper-molybdenum ores composed of chalcosine. enargite and molybdenite (at deeper levels of chalcopyrite); the Central zone with copper ores (chalcopyrite-chalcosine). and the Eastern zone with polymetallic ores composed of chalcopyrite, bornite. galena and sphalerite. Primary ores were subjected to intensive hypergenic alterations that formed an oxidation zone (Cu 1.3%) down to the depth of 200 m, and a zone of secondary sulfide enrichment (Cu 5-2 %) to the depth of 700 m, below which the primary ores (Cu 1.3-1.9%) are located.

Vein Deposits

Vein deposits are rather widespread, though large ones occur rarely. In the USSR these include the Chatyrkul, Zhaisan deposits (Kazakhstan); abroad such deposits are known in Bulgaria (Rosen, Vyrly Bryag), the USA (Butte, Magma), Cuba (Mataambre, El Cobre). and in other countries. The enclosing rocks are frequently represented by granitoids, less often, by volcanogenic, sedimentary and metamorphic formations of different age. The deposits are restricted to shear zones. Ore veins show generally a steep dip and extend along the strike for hundreds of metres-first kilometres (up to 10 km). to the depth from a few hundred to 500-600 m, rarely, up to 1.5 km, their width varying from 0.3 to 10 m and more. The main minerals are chalcopyrite, occasionally enargite; gangue minerals consist of quartz and carbonates (calcite, less commonly, rhodochrosite); subordinate minerals include magnetite, hematite, pyrite, molybdenite, chalcosine, bornite, grey ores, sphalerite, galena. Apart from copper, noble and trace metals are extracted as well.

The ores were formed in several stages at a temperature of 350-200 °C. They are often oxidized at the surface. Among vein deposits

two associations are distinguished, namely, the chalcopyritic and enargite ones, the latter being typical of the large Butte deposit whose characteristics, as an example, is given below.

BUTTE DEPOSIT is located in the USA. For the period from 1882 to 1964 a total of 7.4 mln tons of copper was recovered from the deposit, Zn, Pb, Mo, Ag and Au being extracted as by-products. The deposit is confined to the Upper Cretaceous quartz monzonites (78.4 ± 2 m. y.) which are cut by dikes of the pre-ore quartz porphyry and post-ore liparite. Common in the area of the deposit are pre-ore fractures of the "horse tail" type and post-ore downthrow faults. The ore veins showing a steep dip and a complex structural pattern are united into two systems (Fig. 51): the early, sublatitudinal ("Anakonda", up to 20 veins) and late, northwestern ("Blue veins"). The largest veins are traceable along the strike for up to 9 km, and along the dip for 1.5 km, their average width being over 7-10 m. In swells, where rich chalcosine or rhodochrosite ores are observed, their width attains 30-35 m. Common are chalcosine-enargite, chalcosine-bornite, pyrite-chalcopyrite and pyrite-sphalerite ores. The main minerals are enargite, chalcosine, bornite, chalcopyrite and pyrite; gangue minerals consist of quartz and rhodochrosite; the subordinate minerals include sphalerite, galena, grey ores and native silver. Secondary ores traceable for 100 m and more are represented in the oxidation sone by carbonates, phosphates and copper arsenites; in the cementation zone – by chalcosine and covelline. The ores contain 4-5% Cu and 60-90 ppm Ag. The primary mineral formation developed in three stages: (1) the pre-ore stage resulting in early quartz-molybdenite and quartz-molybdenite-chalcopyrite ores; (2) the major stage when the bulk of the ore was deposited; (3) the post-ore stage when metamorphic alteration of the ore took place accompanied by deposition of alabandine, hematite and chalcedony. The host rocks are sericitized, argillitized and silicified.

According to the data on homogenization of fluid inclusions in the vein quartz of the major stage, the temperature of the ore
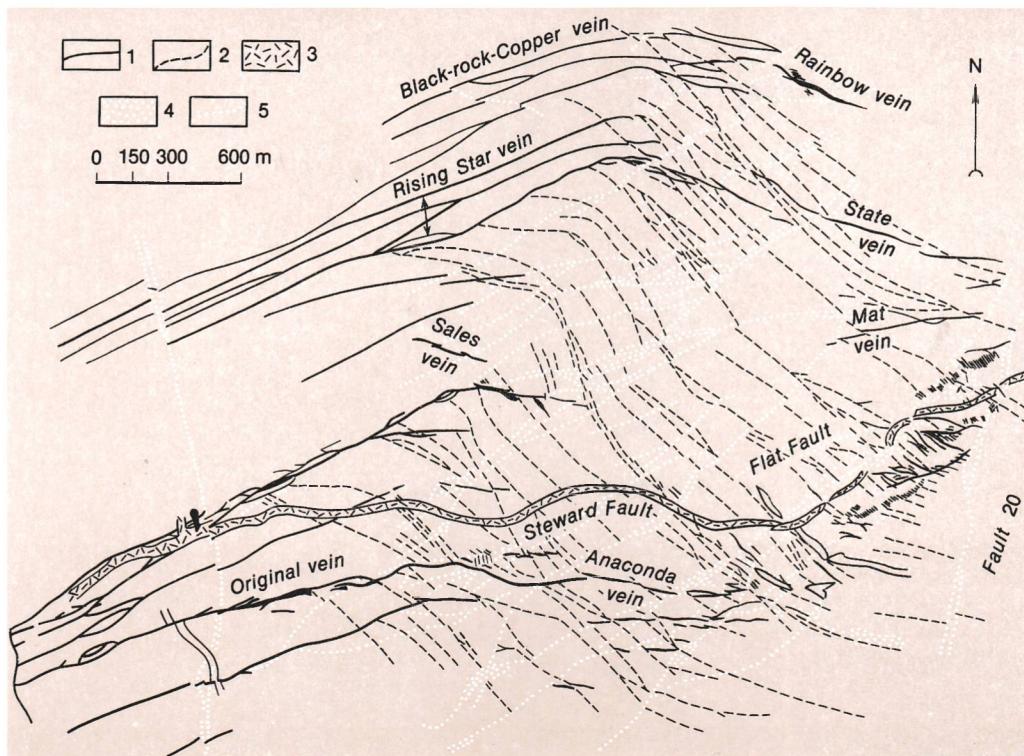
Fig. 51. Geological plan of Butte Deposit. (After G. Meyer):

1 – the first system of veins (Anakonda);   4 – quartz porphyry;
2 – the second system of veins (Sipis);   5 – faults
3 – rhyolite;

emplacement ranges from 350° to 200 °C, being in the peripheral zone 50 °C lower than in the central zone.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

This group of deposits comprises rare occurrences of the native copper formation. Typical is the Lake Superior deposit (USA). In the USSR such occurrences are known in Azerbaijan, the Urals, the Kola Peninsula, Kazakhstan and in the Shoria Mountains.

LAKE SUPERIOR DEPOSIT. A total of 5 mln tons of copper has been mined from the deposits on the Keweenaw Peninsula for 100 years. The area is composed of the Proterozoic volcanogenic sedimentary sequence complicated by linear faults of the north-eastern strike to which subvolcanic gabbro-diabases and associated mineral deposits are confined. The host rocks are represented by amygdaloidal basalts interbedded with conglomerates. Native copper accumulates in amygdules observed in the upper parts of the lava sheets and substitutes the conglomerates. The ores occur as concordant sheet-like bodies whose thickness varies from first metres · to 10-12 m, less frequently, they form crosscutting zones. These have been traced along the strike for 10-12 km and mined to a depth of 2-2.5 km. An association of native copper (rarely silver) with zeolite, calcite, quartz, chlorite, prehnite, datolite and pumpellyite suggests the low-temperature and near-surface conditions of the ore emplacement with a sharp sulphur deficit. Spatially and paragenetically, these ores are likely related to the ancient volcanism, particularly, to the subvolcanic gabbro-diabases.

MASSIVE SULFIDE DEPOSITS

In the USSR copper and copper-zinc massive sulfide deposits are known in the Urals (Gai, Sibai), Mugodzhary (Priorskii) and in the Caucasus (Urup, Kafan); abroad such deposits are known in Turkey (Ergani), the Cyprus (Skurio-Tissa), Bulgaria (Radka), Yugoslavia (Bor), Spain (Rio Tinto), Norway (Leccon), Sweden (Boliden), the USA (United Verde), Canada (Kidd-Creek), Japan (Besi), etc. These deposits are confined to eugeosynclinal sedimentary-volcanogenic sequences of the basaltoid formation of the sodium series as well as to siliceous-terrigeneous strata which are laterally associated with these eugeosynclines. The ore bodies occur in the upper parts of the section of these formations: in volcanic breccia, acid tuffs and volcanic rocks. The mineralization does not spread into the overlying sediments that contain ore fragments. The deposits are controlled by local volcanic structures which represent structural units of the larger volcanic features.

The ore bodies occur as concordant sheet-like bodies and lenses which are composed of massive and bedded ores as well as associated with them (in the footwall) stocks, veins and stockworks of the veinlet-disseminated type. The ore bodies extend for a few kilometres (up to 5 km), their width being tens of metres, occasionally up to 100 m. They are traceable to a depth of hundreds of metres (maximum to 2 km). Two types of ores are distinguished, the volcanogenic-sedimentary ones emplaced under the submarine environments, and the volcanogenic-metasomatic ones formed on the routes of migration of hydrothermal solutions in the host rocks at a depth of tens to hundreds of metres below the sea floor. In the combined deposits both types of ores are observed. They consist of iron sulfides (80-90%) represented by pyrite, melnikovite and marcasite, as well as chalcopyrite, sphalerite or wurtzite, pyrrhotite, less frequently, bornite, grey ores, galena, magnetite, hematite, native gold and silver; the gangue minerals include sericite, chlorite, quartz, barite and calcite. The ores contain up to 40% S, 3-5% Cu, 2-4% Zn; Cd, Se and Te are by-products. The enclosing rocks in the footwall are converted into pyritized quartz-sericite, quartz-sericite-chlorite and other metasomatites.

The massive sulfide deposits were emplaced in the course of 2-3 phases, which are sometimes subdivided into several stages of mineral formation. The first phase is characterized by hydrothermal transformation and pyritization of the enclosing rocks. Iron sulfides were mainly emplaced in the second phase. Chalcopyrite and sphalerite were deposited in the third, most productive phase. The facial and stage-by-stage zonality of the ore bodies is manifested in the change of pyrite (less frequently, pyrrhotite-pyrite with magnetite) ores to pyrite-chalcopyrite and pyrite-chalcopyrite-sphalerite ores in the direction from the foot wall to the hanging wall. The concentric zonality is expressed in a relatively high chalcopyrite content in the central parts of the ore bodies, near the ore feeders, whereas that of sphalerite occurs at their flanks. The secondary zonality manifests itself in an alternation of the following zones (from top to bottom): (1) oxidation (gossan) to a depth of 10-40 m; (2) quartz-barite loose, fine-grained sand (2-3 m-thick); (3) pyrite loose, fine-grained sand (1-3 m-thick); (4) secondary sulfide enrichment with covelline and chalcocite (50-100 m-thick and more) grading into primary ores. The upper zones, especially the second one, are enriched in redeposited gold.

Massive pyrite deposits were formed at the early stages of the geosynclinal development covering a period from the Proterozoic to Alpine metallogenic epochs. The source of copper, zinc and sulphur ($\delta^{34}S$ close to 0) is juvenile, subcrustal. Judging the results of the analyses of inclusions in Japanese massive pyrites, the ore solutions had the following parameters: the temperature (T) varies from 300 to 150 °C, pH – from 3.5 to 5, NaCl concentration – from 0.5 to 3 M, the total content of the dissolved sulphur $\sum S$ – from 10^{-3} to 10^{-2} M, oxygen fugacity fO_2 – from 10^{-38} to 10^{-50} kgf/cm^2.

Deposition of the ore matter is determined by the temperature decrease, the

increase in pH and in $\sum S$, as well as in the increase in fO_2 of gas-hydrothermal solutions in places where the latter flow out and mix with the sea water (R. Large, 1977). This led to the formation of volcanogenic-sedimentary ores which were deposited at the temperature not more than 200 °C, with the water mass thickness being 200 m and temperature of the exhalations of 215 °C.

The deposition of volcanogenic-metasomatic ore in the underlying rocks is characterized by a higher and more variable temperature for different massive sulfide deposits. Hence, we distinguish high-temperature (450 °C and more), medium-temperature (an initial temperature 300 °C, most common deposits) and low-temperature (less than 200 °C) ores (V. Smirnov, 1976).

GAI DEPOSIT is situated in the Southern Urals. The area of the deposit is composed of the sedimentary-volcanogenic sequence which belong to the andesite-dacite-liparite formation of Lower-Middle Devonian. The enclosing rocks are represented by lavas, lava-breccias and pyroclastic rocks of the acid composition, tuffites and cherty schists. These are overlain by the Middle Devonian andesite-basalt formation. Subvolcanic bodies of the acid and basic composition, explosive breccias as well as post-ore dikes and sills of Middle Devonian gabbro-diabases are also widespread.

The Gai deposit is confined to the stratovolcano which is composed of lavas, lava-breccias and volcanic tuffs of the basalt and liparite-dacite composition of the vent and near-vent zone, and of ignimbrite-like rocks. The vent of the volcano is filled with several generations of necks, extrusives and acid subvolcanic bodies. A crater-caldera depression with basaltic lavas, tuff and tuffites occurs above the vent (Fig. 52).

Two groups of ore bodies markedly differing in geological setting, composition and origin are distinguished in the Gai deposit. In the upper part of the deposit there is the so-called "Core lens" which occurs almost as a concordant body of rich zinc-copper massive sulfide ores of the volcanogenic-sedimentary origin filling the volcanic caldera. Below the ore lens lie relatively low-grade massive pyrite and

copper-pyrite ores of the volcano-genic-metasomatic origin which have been traced by the prospecting workings and boreholes to a depth of 2 km. The main minerals of the ores of the first type are: chalcopyrite, sphalerite, pyrite; besides bornite, grey copper ore, galena, quartz, barite, fluorite, carbonate are also observed. The ore structure is massive and banded. The ores of the second type are notable for abundance of pyrite, and in lesser amounts of chalcopyrite. The ore structure is massive, stringer, disseminated. These ores are accompanied by metasomatites containing abundant pyrite dissemination.

The ores of both types have undergone metamorphism of the greenschist facies which caused an emplacement of rege-nerated chalcopyrite-sphalerite-galena-barite veinlets that have penetrated into the surrounding and overlying rocks.

The age of the Gai deposit is synchronous with the time of accumulation of the Lower-Middle Devonian ore-enclosing formation. A vertical scale of the hydrothermal-metasomatic mineralization, as judged by the pressure in the fluid inclusions of quartz, varies from 1 800-2 000 to 3 600-3 800 m. The pressure* at the depth of 200 m from the present-day surface is 560 kgf/cm^2; with a depth increase to 1 200 m it also increases by 250 kgf/cm^2 (G. Pshenichnyi, 1976). The study of the fluid inclusions in sulfides and the associated gangue minerals has shown that in the process of the metasomatic ore emplacement, the temperature regime varied from 400-350 °C (at the early stages) to 170-150 °C (at the final stages). According to the chemical analyses of aqueous extracts, the inclusions show the chloride-bicarbonate composition of the anion part, Mg and Ca (sometimes K and Na) being predominant among cations.

RIO TINTO DEPOSIT is situated in Spain. The deposit area is composed of the Lower Carboniferous rocks 600-800 m-thick. The section starts with basalts substituted up-wards with andesites and ends with a sequence of acid lavas and pyroclasts overlain by schists and greywacke. Lower Carboniferous

---

* Here and further on, 1 kgf/cm^2 = 98.0665 kPa.
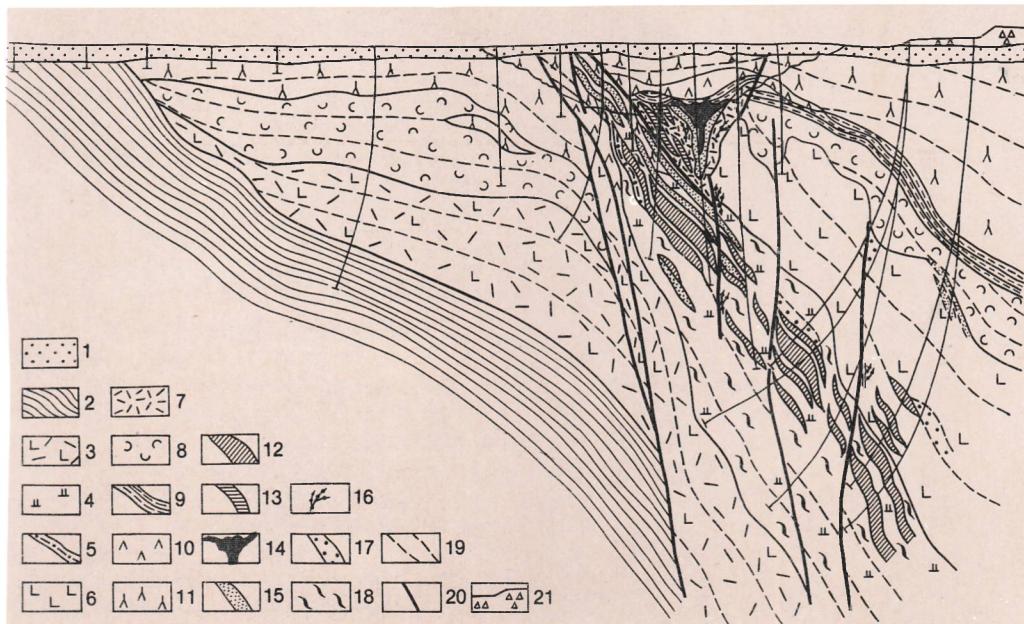
Fig. 52. Geological section through the Gai Deposit. (After M. Borodaevskaya, V. Trebukhin, V. Sementin):

1 – Mesozoic-Cenozoic sandy-clayey sediments;
2 – basement rocks of the Gai paleovolcanic structure – interbedding of cherty and cherty-clayey aleurolites (D_1?). Volcanogenic and volcanogenic-sedimentary rocks of the Gai paleovolcanic structure (D_1-D);
3 – andesite-dacite sequence;
4-5 – liparite sequence: 4 – lavas, clastic lavas, breccia lavas, liparite tuffs, silicified, sericitized pyritized, foliated:
5 – an alteration of siliceous pelitic tuffites, jasperoids, quartz tuff-sandstones and massive pyritic and copper pyritic ores;
6 – dacite sequence (sheet lava, lava of extrusive domes and its fallen agglomerates, pyroclasts);
7-8 – liparite-dacite sequence:
7 – silicified, sericitized and mineralized pyroclasts of liparite composition;
8 – tuffs of liparite-dacite composition interbedded with tuffites, red quartz liparites;
9 – transitional layer (alteration of weathered tuffs with tuff-sandstones, tuffites, slag-tuffs of basalts, chert);

10-11 – basaltoid sequence:
10 – diabase, quartz diabase, gabbro-diabase;
11 – amygdaloidal and slag lavas, lava-breccia; tuff, tuffite of pyroxene-plagioporphyric basalt. Sulfide mineralization. Massive ores:
12 – pyrite and low-grade copper-pyrite;
13 – copper-pyrite and copper-zinc-pyrite showing relatively high copper and zinc contents;
14 – high-grade copper-pyrite (including bornite ore) and copper-zinc-pyrite. Stringer-disseminated ore and products of disintegration of ore bodies;
15 – copper-pyrite and copper-zinc-pyrite stringer-disseminated commercial ore;
16 – stringers and stockworks of chalcopyrite-pyrite and chalcopyrite mineralization representing the zones of redeposited ore;
17 – layers and segments containing the ore clasts of massive pyrite and low-grade copper-pyrite ores. Other symbols:
18 – foliation;
19 – bedding;
20 – synvolcanic long-lived faults;
21 – quarry dumps

rocks fill in the gentle dipping syncline which is complicated by the anticline formed in the place of the volcanic dome structure. The mineralization is confined to this structure being concentrated at the beds of the acid pyroclastic rocks.

The shape of the ore body is complex: in the upper part it occurs as a concordant sheet-like body of massive pyrite-polymetallic ores which are largely eroded,

and below it there is a stockwork of veinlet-disseminated copper pyrite ores (Fig. 53). The sheet-like body extends for several kilometres along the strike being up to first tens of metres thick. Several stockworks are known from the area to attain hundreds of metres across and traceable down to 300 m.

The main minerals of massive sulfide ores are pyrite, chalcopyrite, sphalerite and galena; arsenopyrite, pyrrhotite, burnotite,
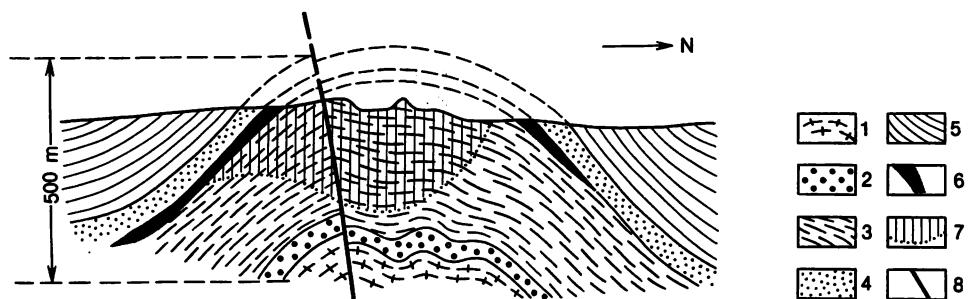
Fig. 53. Schematic section through the Rio Tinto massive sulfide polymetallic deposit. (After V. Smirnov):

1 – basic lavas;
2 – transitional layer with conglomerates;
3 – acid lavas;
4 – acid tuffs;

5 – greywacke-shale rocks;
6 – massive sulfide ore;
7 – ore stockwork;
8 – post-ore fault

tetrahedrite and pyrargyrite are less frequent; gangue minerals are represented by quartz, barite and carbonates. Structures of the ores are massive and bedded owing to thin intercalation of sulfides and tuffites. They contain 1% Cu, 1% Pb and 2% Zn, whereas the gossan formed later contains 25 ppm gold and 45 ppm silver.

Copper pyrite ores of the stockworks consist primarily of pyrite and chalcopyrite and are characterized by veinlet-disseminated and brecciated structures. They have been also subjected to hypergene alterations which have led to formation of secondary (chalcosine) ores with the average copper content being 0.7%. Quartz-sericite-chlorite metasomatites are only common in the foot wall of the sheet-like body, where they are found among the veinlet-disseminated ores.

The Rio Tinto deposit is related to acid differentiates of the Lower Carboniferous volcanism. Veinlet-disseminated copper-pyrite ores were emplaced on the routes of migration of hydrothermal solutions at temperature of 400 °C and below. Where these solutions flow out onto the sea floor under the submarine environments at the temperature of 100 °C and below, the bedded massive sulfide ores of the hydrothermal-sedimentary origin were formed (V. Smirnov, 1978).

STRATIFORM DEPOSITS

These include bedded ores of copper which occur in the terrigenous sequences and do not show any relation to magmatic rocks.

They are represented by large deposits of cupriferous sandstones and cupriferous shales. The cupriferous sandstones are known both in the USSR (Kazakhstan-Dzhezkazgan, Baikal region – Udokan) and abroad – in Zambia (Roan-Antilope, Chambezi, Nchanga), Zair (Komoto, Musoshi) and Afghanistan (Inak). The cupriferous shales occur in the GDR (Mansfeld) and Poland (Fore-Sudeten). The stratiform deposits are formed at the final stages of the geosynclinal regime and under platform conditions. They are confined to the depressions filled with rhythmically inter-bedded sandstones, shales and dolomites of lagoon-delta and near-shore facies. These rocks, characterized by a relatively high content of organic carbon (over 2%), compose the initial transgressive or final regressive parts of the section.

These ores occur as concordant sheets, lenticular and ribbon bodies usually gently dipping. Their width varies from tens of centimentres to first tens of metres; they extend for many kilometres along the strike and for a few kilometres along the dip. Typical are multi-stage bodies showing gradual transitions to weakly mineralized rocks. Locally, there occur cross-cutting ore veins and crush zones. The main ore minerals are chalcocite, bornite, chalcopyrite, pyrite; the subordinate minerals include copper grey ores and covellite, in some places galena, sphalerite, etc.; the gangue minerals are represented by quartz, calcite and barite. Pb, Zn, Ag and trace

...ments. occasionally cobalt and uranium ... cupriferous sandstones of Africa) are by-... ducts. The enclosing rocks are weakly ... (carbonatized, silicified).

...he zonality across the thickness of the ... bodies is manifested in: (1) restriction of ... copper ore to the lower parts of the ... (terrigenous rocks), and the lead-zinc ... to its upper parts (carbonate rocks); ... mineral associations change from bottom ... up in the following order: chalcocite-... te-chalcopyrite-pyrite (Dzhezkazgan) or ... versa (Udokan, Roan-Antilope). A ... zonality is thought to be a result of ... gressive accumulation of cupriferous ... ments and a reverse zonality – of ... gressive accumulation. The lateral zonality ... expressed by a successive substitution ... sulfides of copper, lead and zinc ... ng the dip of the ore bodies as ... enclosing sediments grade from shallow ... deep-water facies. This zonality is also ... firmed by the restriction of the bornite-... lcocite ores to the coarse-grained sedi-... ments of the delta facies and the pyrite-... lcopyrite ores – to the fine-grained varie-... es of the deeper marine facies.

The main stratiform copper deposits were ... med in the Proterozoic and Upper Paleozoic time. Many geologists consider ... em to be syngenetic, initially sedimentary, ... iously metamorphosed. This is supported ... a stratified pattern and a wide areal distribution of the mineralization, the ... sence of genetic relations with intrusions, ... concordant sheet-like shape of the ore ... dies. rhythmic and multi-stage pattern of ... eir structure which is caused by their ... nfinement to certain facies of sediments, ... simple mineral composition of the ores, ... presence of bedding structures and glob-... lar textures in the ores, low temperatures ... mineral formation (usually less than ... C). correlation of metal concentration ... ith the organic carbon, development of sul-... phur isotopes of the "biogenic" origin, etc. Two possible sources of metals may be ... pposed: (1) the areas where parent rocks ... ontaining copper occurrence are being ... oded, and (2) volcanic exhalations and ... drotherms.

Some of the deposits of cupriferous ... andstones (for example, Dzhezkazgan)
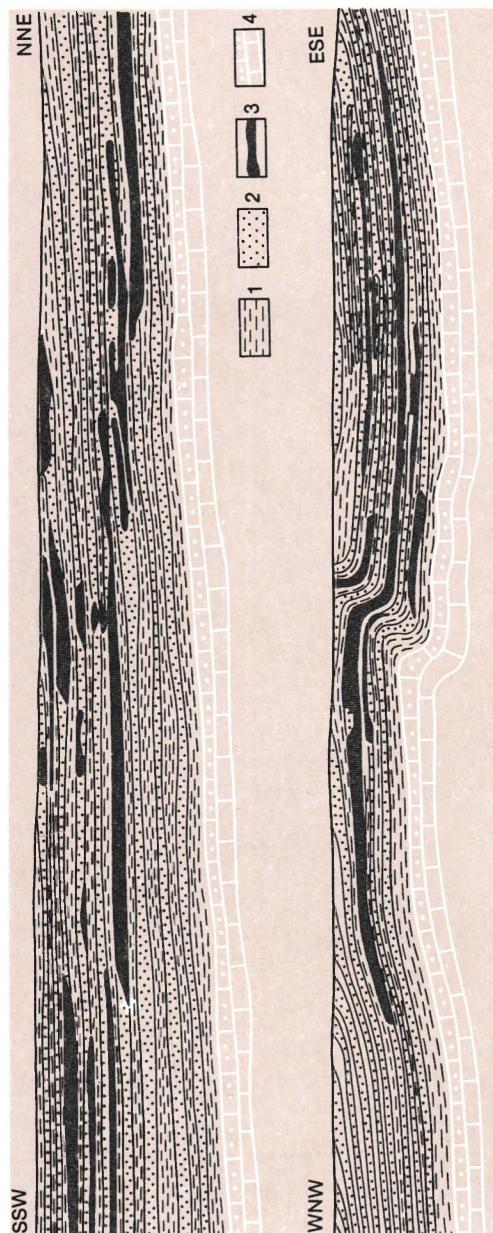
Fig. 54. Schematic geological sections through the Dzhezkazgan deposit (from the data of the Dzhezkazgan Geological Prospecting Expedition):

1-3 – Dzhezkazgan formation of Middle-Upper Carboniferous: *1* – red sandstone and siltstone; *2* – ore-bearing layers of gray sandstone, aleurolite and conglomerate; *3* – ore bodies; *4* – limestone, sandstone, marl of Lower Carboniferous

exhibit the features that contradict their syngenetic origin. These are: structural control of rich ores, a stage-by-stage pattern of mineral formation, a relatively high formation temperature (from 200° to 70°C) according to the data on the fluid inclusions and hydrothermal alteration of the host rocks. That is why some investigators consider these deposits as epigenetic infiltration, hydatogenic (A. Germanov, A. Perelman, I. Gablina), or as magmatogenic hydrothermal (K. Satpaev, Sh. Esenov) types. The hypothesis is being elaborated at present suggesting the polygenic and polychronous origin of the stratiform deposits in which primary syngenetic ores of the sedimentary genesis have been transformed under the influence of diagenesis and catagenesis, and later subjected to the effect of underground hot mineralized waters (V. Smirnov, 1976).

DZHEZKAZGAN DEPOSIT is located in Kazakhstan. It is composed of the Middle-Upper Carboniferous molasse, 600-700 m thick, consisting of rhythmically intercalated grey and red sandstones, siltstones and mudstones. The deposit is confined to the Dzhezkazgan syncline in the zone of its junction with the Kingir anticline formed in the place of the paleouplift.

The mineralization occurs as gently dipping concordant bodies of disseminated ore (Fig. 54). The bodies exhibit a sheet-like and lenticular shapes at the surface and a ribbon shape at depth. They are mainly confined to the grey sandstones that form nine ore-bearing beds. A total up to 100 ore bodies, from 0.5 to 20 m-thick, are known to occur in these beds. The lenticular bodies extend for a few kilometres, the width being 100-200 m. They are traceable to the depth of 600 m. Transverse zones of crush and jointing appear occasionally to be also mineralized. The main minerals are chalcocite, bornite, chalcopyrite, galena and sphalerite; the gangue minerals include quartz, calcite and barite; the subordinate minerals are represented by pyrite, covellite, grey ores and hematite; among the rare minerals there is a rhenium mineral dzhezkazganite $Re(MO)_2$. The ore is usually characterized by a disseminated type of structures less frequently, stringer ones. The textures are those of mutual boundaries, of

intergrowth, of replacement, micrographic, emulsion and relict (globular, crustificational). Apart from copper, the ores contain Pb, Zn, Re and noble metals. Mineral formation occurred in two stages: the early stage, when fine-grained sulfides, chalcocite and others, were deposited, and the late stage, in which coarse-crystalline aggregates of chalcocite, galena and sphalerite of the stringer ores were formed. Alterations of the enclosing rocks, namely, carbonatization, silicification and albitization, as well as the grey colour of the rocks are caused either by deep-seated epigenesis, or hydrothermal metamorphism.

The mineral zonality in ribbon-shaped bodies is expressed by the change of sulfides from the lower part upwards and towards the periphery in the following order: chalcocite – bornite – chalcopyrite – pyrite – galena – sphalerite. In sheet and lenticular bodies a change of bornite ores to pyrite-chalcopyrite ones is observed from the centre towards the periphery. The ratio $\dfrac{Re}{Os}$ helps to date the mineralization at 260 m.y. (G. Shcherba, et al, 1976). As judged by the relict textures jarleite and x-bornite association started to form at the temperature of less than 75°C. Later, under the influence of heated underground waters, the temperature rose to 140–150°C causing x-bornite to disintegrate (I. Gablina, 1976). Disseminated ores are characterized by the uniform isotopic composition of sulphur ($\delta^{34}S$ from -10.4 to -17.7%), unlike the veined ores ($\delta^{34}S$ from -27.4 to $+17.3\%$). The formation of the Dzhezkazgan ores is probably a long and complex process. Disseminated ore mineralization is associated with the sedimentation; afterwards, in the process of diagenesis and deep epigenesis, there occurred a certain concentration of the ore matter, and finally, under the influence of the hot mineralized solutions, the stringer and vein types of ores were formed (G. Shcherba et al, 1976).

UDOKAN DEPOSIT is situated in the Northern Baikal region. The deposit area is composed of a sequence of metamorphosed miogeosynclinal carbonate-terrigenous rocks of the Lower Proterozoic Udokan series. The ore-bearing strata 20-330 m thick, are
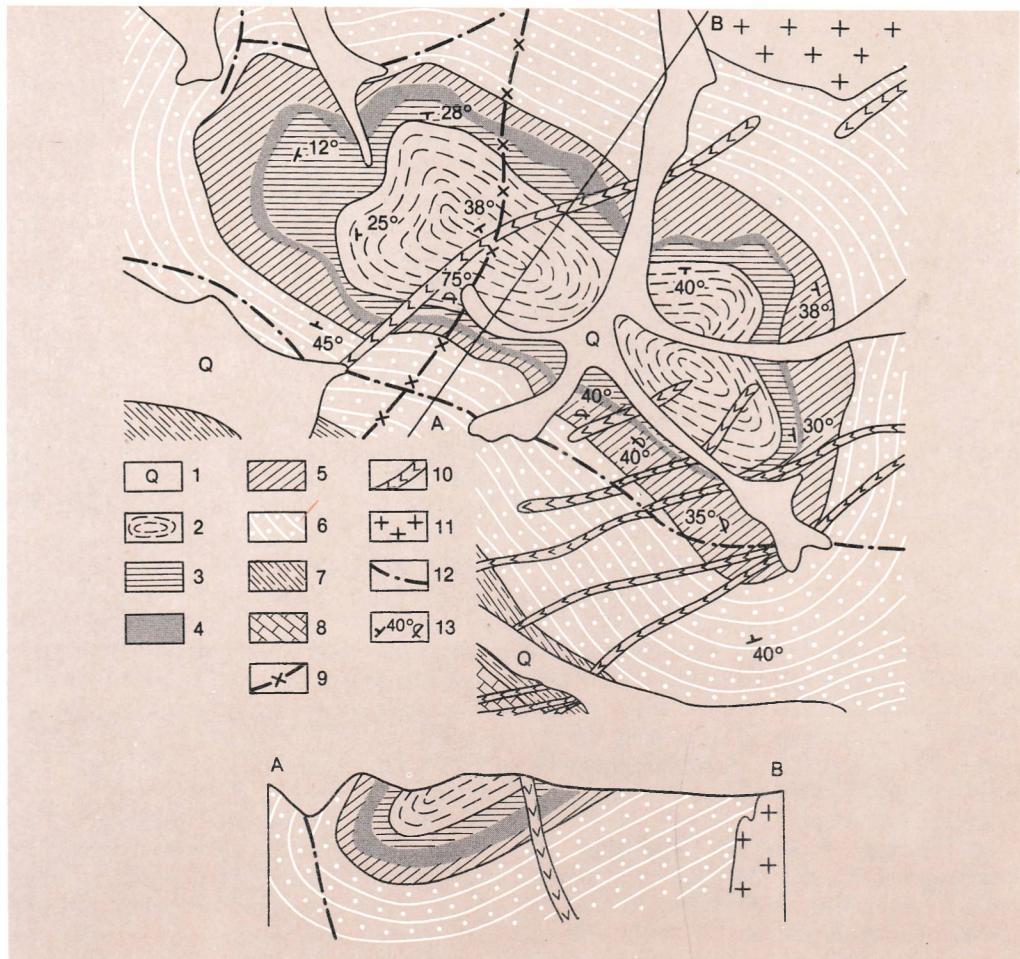
Fig. 55. Geological sketch map of the Udokan deposit. (After E. Grintal and V. Chechetkin):

1 – Quaternary sediments;
2 – Namingin formation – aleurolites, sandstones, argillites;
3-5 – upper member of Sakukan formation:
3 – supra-ore beds (calcareous and quartzite sandstones, aleurolites);
4 – ore beds (calcareous and quartzite-like sandstones, aleurolites);
5 – sub-ore beds (quartzite-like and limy sandstones, aleurolites, conglomerate-breccias);
6 – middle member of Sakukan formation – magnetite-bearing sandstones, gravelstones;

7 – lower member of Sakukan formation – sandstones, phyllite-like schists, gravelstones, conglomerate-breccias;
8 – Butun formation – limestones, siltstones, calcareous sandstones;
9 – dikes of granosyenite-porhyry;
10 – dikes of gabbro-diabase;
11 – granite of Chuya-Kodar complex;
12 – faults;
13 – dip and strike of beds

composed of the rhythmically interbedded rocks of the delta and shallow-marine facies consisting (from bottom to top) of: conglomerate-breccia, essentially quartz sandstone with calcareous cement and aleurolite frequently exhibiting cross-bedding. The deposit is confined to the Namingin brachysyncline (15 km long) showing a N-vergence (Fig. 55). This feature is complicated by folds and faults to which gabbro-diabase dikes are confined.

The ore bodies have concordant sheet-like, lenticular and ribbon-like shapes. The rich bodies are confined to the eroded surfaces in local depressions and in river channel troughs and are traceable along thé

strike for 2-3 km. Three types of ores are distinguished: pyrite-chalcopyrite, chalcopyrite-bornite and bornite-chalcocite. The ores are represented by quartzose sandstone or aleurolite with fine (tenth to hundredth fractions of a millimetre) sulfide impregnation. The main minerals are chalcocite, bornite, chalcopyrite and pyrite; the subordinate ones include magnetite and hematite. The ores are monometallic (copper ones with silver admixture). The ore structures are disseminated, bedded, mottled, brecciated and stringer-disseminated; the ore textures are of the mortar, allotriomorphic-granular, graphic, lattice, emulsion, reticulate and intersertal types.

In the vertical section of the cupriferous sequence, four zonal series of the regressive type are recognized, each exhibiting/ a change (from bottom to top) of pyrite-chalcopyrite ores to bornite-chalcocite ones; in places the vertical zonality appears to be reverse, of the transgressive type. The horizontal zonality is expressed by the fact that bornite-chalcocite ores tend to be localized mainly at the coastal zone (in the north), whereas the pyrite-chalcopyrite ores – at the deep-water parts of the lagoon basin (in the south).

Four stages of the ore deposition are distinguished. During the first two stages, sedimentation and catagenetic, the main commercial types of the ore were formed. These ores were metamorphosed during the subsequent stages. First the ores were subjected to regional metamorphism and then to contact-metamorphic transformations. The regional metamorphism of the greenshist facies resulted in recrystallization of the cement in the sandstones, regeneration of the ore minerals and formation of quartz-sulfide veins at the temperature of 300-400 °C (according to the decrepitation data). The contact-metamorphic process related to the dikes of gabbro-diabases caused a more intensive sulfide regeneration and appearance in the near-contact zone of small but rich quartz-sulfide bodies with the temperature of the emplacement being 300-450 °C. The Udokan ores are characterized by the $\delta^{34}S$ range from $+13.5$ to -21.8% with the sharp increase in the number of the light isotopes, which points to the biogenetic origin of sulphur.

NCHANGA DEPOSIT is located in Zambia, in the Central Africa Copper Belt, extending for 600 km along the border between Zair and Zambia, mainly on the territory of the latter. The copper reserves at the Nchanga deposit are estimated at 9 mln tons, the copper content being 3.95%. The deposit area is composed of conglomerate, quartzite, arkose sandstone and calcareous schists of the Lower Proterozoic. They overlie unconformably granites of the basement forming a syncline (Fig. 56). The ore bodies are represented by concordant sheet-like bodies of the total thickness up to 100 m. The main minerals of the primary ores are chalcopyrite, bornite and chalcocite; the subordinate minerals are represented by pyrite and millerite. They occur as a fine impregnation and together with quartz they form veinlets and veins. The zones of oxidation and secondary enrichment traceable to the depth of several hundreds of metres are composed of malachite, cuprite, bornite as well as azurite, native copper, chrysocolla, torbernite. The enclosing rocks are dolomitized.

A zonality through the thickness of ore bodies (mineralized sandstone and underlying shales) manifests itself in the substitution (from top to bottom) of pyrite, first by chalcopyrite and then by bornite. The horizontal zonality is expressed in the fact that the central part of ore bodies is composed of bornite and chalcopyrite, the middle part consists of chalcopyrite (with linneite), and the peripheral part of pyrite. The deposit is dated as Lower Proterozoic; its genesis is sedimentary with a subsequent metamorphic and hydrothermal alteration.

FORE-SUDETEN DEPOSIT is located in Poland within the Fore-Sudeten monocline composed of the platform sedimentary cover. The area is noted for red and partially light grey sandstones of the Lower Permian and Upper Permian age. The latter are represented (from bottom to top) by black bituminous shales (up to 1.5 m in thickness), dolomites and limestones (up to 90 m), followed by a thick anhydrite and rock salt unit. Mineralization is confined to the Lower Permian light grey sandstones,
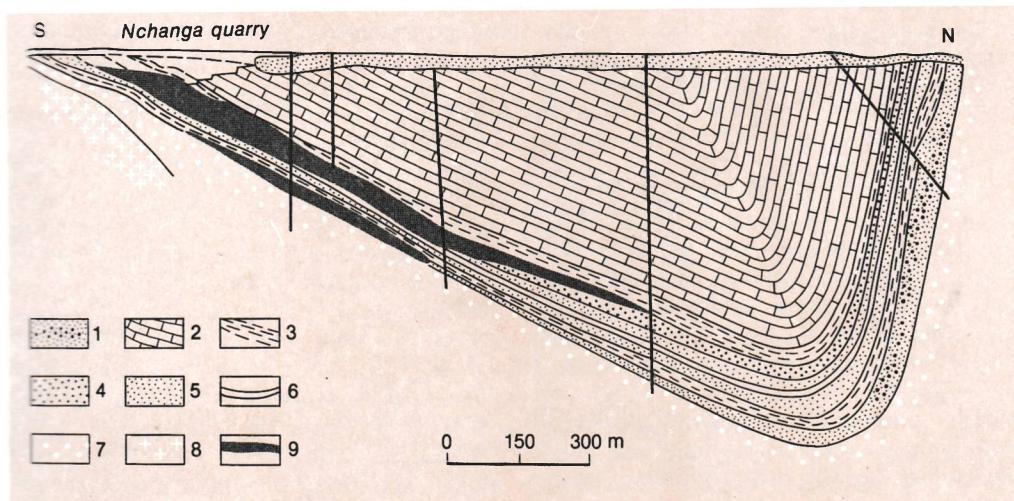
Fig. 56. Geological section through the Nchanga syncline. (After F. Mendelson):

1 – beds of detrital quartz and surface deposits;
2 – argillites and dolomites;
3 – banded shales;
4 – feldspar quartzites;
5 – banded sandstone beds;
6 – quartzites and chert;
7 – arkose sandstones;
8 – granite;
9 – ore bodies

Upper Permian black shales and dolomites which are regarded as the lagoon and delta facies. Copper-bearing rocks gently dipping eastward have been traced by boreholes for ~ km along the strike and for 10 km along the dip. They are complicated by post-ore faults varying in amplitude from 20 to 40 m.

Ores occur as concordant sheet-like bodies varying in width from several to ~15 m. There is a distinct confinement of mineralization to the rocks enriched in organic matter whose average content in sandstones is 0.31%, in shales, that comprise the richest ores, it is 4.3%, and in carbonate rocks. 0.54%. Main ore minerals include chalcocite, chalcopyrite and bornite; subordinate minerals are represented by pyrite, covelline, grey ore, sphalerite, galena, arsenopyrite, linneite; in the oxidation zone these are malachite, azurite, cuprite, tenorite, native copper, smithsonite, cerussite. The ores contain copper, lead, zinc and silver as well as an admixture of cobalt, nickel, molybdenum, vanadium, tin and rhenium. The ore structures are banded, impregnated, rarely stringer; the impregnation is very minute (units – tenths of microns).

The textures are of mutual boundaries, globular, emulsion, rarely of replacement and corrosive. A zonality through the thickness of ore bodies consists in a change of the maximum mineral accumulations in a direction from the footwall to the hanging wall in the following order: chalcocite – bornite – chalcopyrite – pyrite – galena – sphalerite; copper tends to accumulate at the lower beds (sandstones and especially shales), lead and zinc, are confined, respectively, to the middle and uppermost parts of the succession, composed of carbonate rocks. Along the dip of the ore bodies the chalcocite is replaced by bornite, then by chalcopyrite.

Some geologists (E. Konstantinovich) consider the deposit to be syngenetic, sedimentary, others (like Ya. Vyzhikovsky) attribute it to the hydrothermal-sedimentary types. In the first case, disintegrated rocks and Hercynian ore occurrences of the Sudeten Mountains are believed to be a sorce of copper; in the second case, this source could be represented by underwater exhalations related to the Early Permian volcanism.

11 LEAD AND ZINC DEPOSITS

Lead was known in Mesopotamia and Egypt as far back as 6000-7000 B.C. The first bronze in Central Asia was an alloy of copper and lead.

The latter is an integrated part of alloys used in production of batteries, cables and bearings, in printing business; it is also used for production of gasoline antidetonator. Oxidized zinc ores were used at the ancient times in smelting copper, bronze and brass, but as a metal zinc was only obtained in 1746 by the German chemist A. Marggraf. Nowadays zinc is used for galvanization of metal articles, for production of alloys (brass, bronze), zinc whites, in electronics and industrial engineering.

Lead and zinc occur together with other metals (copper, gold, silver) forming base metal (polymetallic) deposits. There are lead and zinc deposits with a variable ratio of these metals.

Less common are specific zinc and lead ore deposits.

The price of one ton of lead is 745 US dollars, that of zinc 475 US dollars. In 1975 the capitalist and developing countries produced 2400000 tons of lead and 4395000 tons of zinc; the prospected reserves of lead and zinc made up 110 million and 137 million tons, respectively, the total lead and zinc reserves are respectively 135 million and 215 million tons.

Unique deposits (Broken Hill in Australia) possess over 5 million tons of the lead and zinc reserves; the reserves of very large deposits vary from 5 to 2 million tons, those of the large ones are 2 million to 600000 tons, the reserves of average deposits range from 600000 to 200000 tons, and those of minor deposits are under 200000 tons. The lead content in high-grade ores is over 5% (sulfides), in ordinary ores – from 5 to 2%, and in low-grade ores – less than 2%. The total lead and zinc content in high-grade ores exceeds 7%, in ordinary ores – from 7 to 4%, and in low-grade – under 4%.

GEOCHEMISTRY AND MINERALOGY

There are four stable lead isotopes with mass numbers 204 and 206-208, the ^{208}Pb (52.1%) being predominant. Isotopes ^{206}Pb, ^{207}Pb and ^{208}Pb are the end stable products of decay of U (Ra), Ac and Th. Zinc has five stable isotopes with mass numbers 64, 66-78 and 70, among which ^{64}Zn (48.9%) is predominant.

Lead crustal abundance (clarke) is $1.6 \cdot 10^{-3}\%$; concentration coefficient is 2000. The lead crustal abundance increases from ultrabasic $(1 \cdot 10^{-5}\%)$ and basic $(8 \cdot 10^{-4}\%)$ to acid magmatic rocks $(2 \cdot 10^{-3}\%)$. The zinc crustal abundance (clarke) is somewhat higher: $8.3 \cdot 10^{-3}\%$; concentration coefficient is 500. The zinc crustal abundance for magmatic rocks increases from ultrabasic $(3 \cdot 10^{-3}\%)$ to basic $(1.3 \cdot 10^{-2}\%)$ varieties; for intermediate $(7.2 \cdot 10^{-3}\%)$ and acid $(6 \cdot 10^{-3}\%)$ rocks it is close to the total crustal abundance.

Lead and zinc concentrate in residual portions of acid differentiates of the basaltic and granitic magma. These metals are transported by hydrothermal solutions in the form of complex compounds. N. Baranova has experimentally established that in the H_2S-free solutions at a temperature of 300-250°C and pH = 4-6 the lead is present in the form of chloride complexes $(PbCl^+)$ with small amounts of sulphate $(PbSO_2^0)$ and fluoride (PbF^+) complexes, while with pH = 6-8 it also migrates in the form of carbonate complexes $(PbCO_3^0)$; at a temperature of 200-150°C in aqueous solution with pH = 4-6 sulphate complexes dominate and with pH = 6-8 – carbonate ones. In the H_2S-containing solutions at a temperature of 300-250°C and at the pH range of 4-8 the $Pb(HS)_2^0$ and $Pb(HS)_3^-$ hydrosulfides are prevailing; at the temperature of 200-150°C and pH = 4-6 the lead occurs as sulphate complexes, while at pH = 6-8 it is present in the form of carbonate complexes with a small amount of hydrosulfide complexes. Galenite may precipitate at any temperature in the solutions with pH > 3, providing the total concentration of H_2S exceeds its lower

limit at the corresponding temperature. Like lead, zinc is transported either by chloride ($ZnCl_2^0$) or sulfide complexes ($ZnHS_2^-$).

Under exogenous conditions lead and zinc sulfides are oxidized to form sulphates. Zinc sulphate is an easily soluble compound (500 000 gr in 1 m^3 of water) and can readily migrate, but zinc in this case could be redeposited in the form of secondary carbonates. Lead sulphate does not easily solve and lead does not migrate from the oxidation zone. Metamorphic processes do not cause any appreciable migration of lead and zinc.

Main lead minerals include galena PbS (86.6%), commonly with Sb, Bi and Ag admixture, jemsonite $Pb_4FeSb_6S_{14}$ (40.16%), boulangerite $Pb_5Sb_4S_{11}$ (55.42%), burnonite $CuPbSbS_3$ (42.6%); and cerussite $PbCO_3$ (77.6%) with anglezite $PbSO_4$ (68.3%) in the oxidation zone. The main zinc minerals are sphalerite ZnS (67%) with an admixture of Cd, In, Ga and Ge, wurtzite ZnS hex. (63%), and smithsonite $ZnCO_3$ (52%), calamine Zn $[Si_2O_7]$ $(OH)_2$ (53.7%) in the oxidation zone. Galena and sphalerite are the main commercial minerals of lead-zinc ores.

METALLOGENY

At the early stage of the geosynclinal cycle, in relation to acid differentiates of a basaltoid volcanism, massive sulfide deposits were formed, the oldest of which were subsequently strongly metamorphosed. At the later stage involving reactivation of platforms and ancient folded regions various medium-scale deposits were formed, including skarn deposits at exocontacts of granitoid intrusions and plutonogenic hydrothermal deposits such as metasomatic in carbonate rocks, veined in granitoids and metamorphic rocks and volcanogenic hydrothermal deposits related to andesite-rhyolite formations. The geosynclinal and especially platform cycles culminated in the formation of large lead-zinc ore stratiform deposits confined to carbonate sequences developed within uplifts and in gentle troughs.

Lead and zinc deposits developed in various geological epochs: Proterozoic (Kholodninsk and Gorevskii in the USSR), (Broken Hill in Australia), Caledonian and Hercynian (Ozernyi, Ridder-Sokolnyi, Zhairem in the USSR; Freiberg in GDR), Kimmerian and Alpine (Filizchai, Zgid in the USSR; Rio Tinto in Spain; Kuroko in Japan).

TYPES OF COMMERCIAL DEPOSITS

The following commercial types of lead and zinc deposits are recognized; (1) skarn; (2) plutonogenic hydrothermal; (3) volcanogenic hydrothermal; (4) massive sulfide; (5) stratiform; (6) metamorphosed.

SKARN DEPOSITS

Lead and zinc skarn deposits are known in the Soviet Union from Primorski Krai (Verkhnii, Nikolayevskii), Kazakhstan (Kyzyl-Espe, Askoran), Central Asia (Altyn-Topkan, Kansai), in other countries: in Yugoslavia (Stary Trig), Sweden (Sala, Ammaberg), the USA (Franklin-Fernas, Lawrence), Mexico (El-Potosí), Argentina (Agillar), China (Tembushan) and Japan (Kamiona). The deposits are related to granitoids of hypabyssal facies (granodiorite-porphyry, granite-porphyry). They occur either at the contact, or at the exocontact zone of intrusives and enclosing sedimentary or volcanogenic-sedimentary strata that comprise limestone beds. They are controlled by faults, interformational detachments and fissure zones. Skarn deposits occur as sheet-, lens- or vein-like bodies, have a thickness of tens of metres and extend for many hundreds of metres. However, the morphology of lead-zinc sulfide ores superimposed on lime skarns of the garnet-pyroxene composition is more complex. The ores occur as lenses, column-like bodies and pockets. The ore bodies extend for hundred metres along the strike and along the dip, their thickness varies from 1 to 10 m and more. The mineral composition of ores of the skarn deposits is presented by a combination of skarn-forming silicates and sulfides. The emplacement of ore involved several phases among which the most important were the pre-ore skarn (800-600 °C), productive sulfide or galena-sphalerite (240-150 °C) and post-ore quartz-calcite phases (80-50 °C).
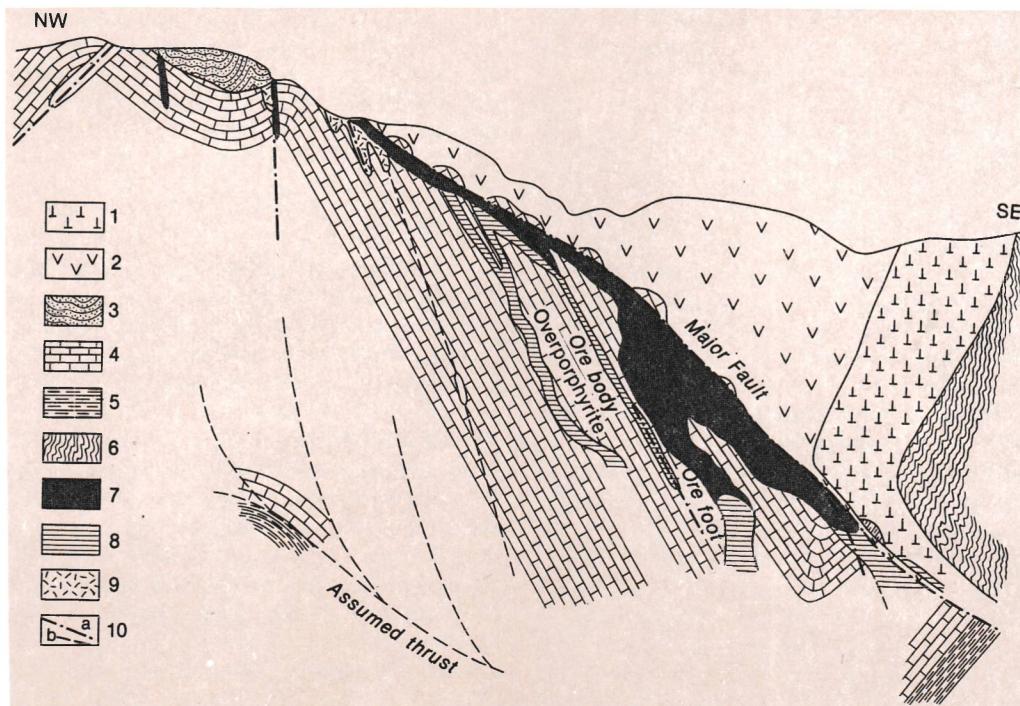
Fig. 57. Schematic geological section through the Verkhnii deposit. (After I. Tomson and N. Mozgovoi):

1 – andesite;
2 – quartz porphyry;
3 – siliceous sandy-shaly rocks;
4 – limestone;
5 – sandy-shaly rocks;

6 – chert;
7 – ore body in skarns;
8 – projection of the ore body;
9 – oxidized ore;
10 – faults (*a* – certain, *b* – supposed)

VERKHNII DEPOSIT is located in Primorski Krai. The area is composed of Upper Triassic limestones. These are in contact with the Upper Cretaceous quartz porphyry along the Major Fault. There also are intra-ore dikes of Paleogene diorite and diabase porphyries. Mineralization is confined to an overthrust zone (Fig. 57). The main ore body has a form of a branching pipe somewhat flattened out and elongated along the Major Fault. Near the surface the ore body is split into three branches which, at the middle levels merge into two columns, and at depth form a single large ore body. On the surface the ore body extends for 250 m; the main body is traced vertically for 600 m.

The main ore minerals include sphalerite, galena and pyrrhotite; gangue minerals are represented by hedenbergite, quartz and calcite; chalcopyrite, galenobismuthite, arse-nopyrite, pyrite, marcasite, datolite, as well as axinite, garnet, vollastonite, ilvaite, fluorite, siderite, epidote, zoisite, apophyllite, hisingerite, stilpnomelane and dickite are subordinate. Galmey ores are developed in the oxidation zone (at a depth of some tens of meters). The ore structures are massive, banded, spheroidal and drusy; the textures are coarse-crystalline, radiated, metacolloidal and colloform. Host rock alterations consist in pre-ore skarnization and near-ore epidotization, chloritization and carbonatization.

The mineral formation involved four plases: (1) the pre-ore skarn – wollastonite-garnet phase (over 600 °C); (2) skarn-sulfide phase (600-400 °C); (3) sphalerite-galena phase (350-120 °C); (4) chalcedony-calcite phase (100-20 °C), whose minerals were deposited as druses in open cavities. The following vertical facies zonality (from top to bottom) is observed: (1) coarse-aggregate hedenber-

gite grades into a fine-grained variety, axinite becomes more abundant; (2) a sphalerite to galena ratio increases; (3) the total metal concentration decreases.

The age of the deposits is Paleogene; the ores precipitated from colloform solutions, which is confirmed by the residual parent solution with a jelly-like silica gel that has been preserved in open cavities.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal lead and zinc deposits are known in the Soviet Union from Transbaikalia (Ekaterino-Blagodat', Kadainsk), Central Asia (Kurgashinkan, Granitogorskii), the Caucasus (Sadon, Zgid), and abroad in Bulgaria (Govedarnik, Ruen), Romania (Baia-Mare), Czechoslovakia (Pshibram), Hungary (Djendyeshoroshi), the GDR (Freiberg), India (Agnigunduna), the USA (Kerr-d'Alen, Tintic, Leadville) and Canada (Cann-Hill). Common in the area of the deposits are granitoids and minor intrusions of the hypabyssal facies which occur as granodiorite-porphyries or granite-porphyry as well as dolerite-porphyry and diabase porphyry dikes. Mineralization is apparently related to the intrusive complexes not only spatially but also paragenetically. The ores occur as sheets, lenses, pipes, veins and stockworks. These are traceable for tens and hundreds of metres (lodes extend for (1.5-2 km) along the strike and the dip, the thickness varying from 0.5 to 200 m and more.

Main ore minerals include pyrite, pyrrhotite, sphalerite, galena, arsenopyrite, marcasite, boulanjerite and jemsonite; quartz, calcite and dolomite represent gangue minerals. Two ore formations are distinguished in plutonogenic hydrothermal lead and zinc deposits: (1) metasomatic pyrite-galena-sphalerite, associated with carbonate rocks (Ekaterino-Blagodat' in the USSR; Tintic in the USA) and (2) vein galena-sphalerite, associated with granitoids and schists (Zgid in the USSR; Freiberg in the GDR).

Metasomatic Deposits of
Pyrite-galena-sphalerite
Formation in Carbonate Rocks

BLAGODAT' AND EKATERINO-BLAGODAT' DEPOSITS are located in Transbaikal region some hundred metres apart from each other and merge at a depth of 500-600 m. The area is composed of a carbonate sequence of Lower Cambrian subdivided into five horizons. Ore bodies are confined to the third horizon made up of several varieties of dolomites and calcareous dolomites. Above them occurs a set of shale beds serving as a screen for hydrothermal solutions. Dikes of quartz porphyry and lamprophyre of the Middle-Upper Jurassic age (140-150 mln years) are also observed. The Cambrian rocks form a syncline with the mineral deposits being located at its limbs (Fig. 58). The fold is complicated by faults that have produced numerous fractures, shear and foliation zones, which control the mineralization.

Ore bodies have a shape of pipes, veins and, more rarely, lenses. Main ore minerals include galena, sphalerite, pyrite, arsenopyrite and stannite; quartz and dolomite are gangue minerals; marcasite, bournonite, meneghinite, grey ores, antimonite, cassiterite and pyrrhotite as well as calcite, ankerite and siderite are subordinate. The oxidation zone is represented by anglesite, cerussite, smithsonite and iron hydroxides. The ore structures are massive, banded and brecciated, the textures are coarse-crystalline and fine-grained. Host rock hydrothermal alterations consist in silicification and dolomitization.

The mineral formation involved three phases: (1) quartz-sphalerite; (2) sulphoantimonite-galena-dolomite; (3) post-ore ankerite-siderite-dolomite. The vertical zonality distinctly manifests itself in pipe-like ore bodies: deep levels are essentially composed of pyrite ores, the intermediate levels – of pyrite-sphalerite ores ($Zn:Pb = 2.4$) and upper levels consist essentially of galena ($Zn:Pb = 1.5$).

The deposits are of the Late Jurassic age because the Lower-Middle Jurassic dikes are the pre-ore features, and the Lower Cretaceous rocks contain fragments of ores and dike rocks.
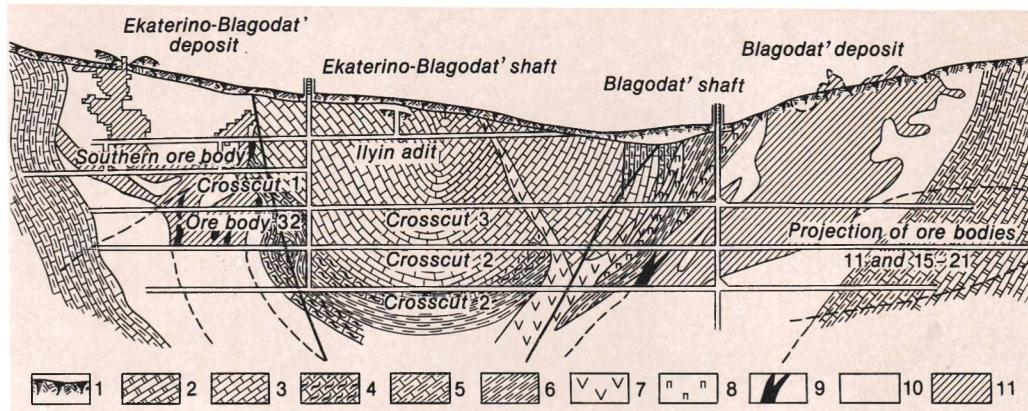
FIG. 58. Geological section through the Ekaterino-Blagodat' and Blagodat' deposits. (After A. Kulagashev and V. Favorov):

1 – loose sediments;
2 – medium-grained dolomites;
3 – fine-grained dolomites;
4 – marly dolomites;
5 – carbonaceous dolomites;
6 – coaly shales;
7 – porphyry;
8 – lamprophyre;
9 – ore bodies;
10 – ore-bearing zone;
11 – mined areas

Vein Deposits of Galena-sphalerite Formation

ZGID DEPOSIT is located in the Caucasus. The area is composed of Paleozoic granites unconformably overlain by Jurassic shales and volcanic rocks. These are cut by a 100 m-amplitude strike-slip fault of the north-eastern trend and steep dip. The ore body is confined to the strike-slip fault and occurs as a vein in granites extending into Jurassic sediments (Fig. 59). Within the vein there are ore columns confined to the points in which the ore-enclosing strike-slip fault intersects the pre-ore NW-trending transverse faults with minor post-ore displacements. Main ore minerals include galena and sphalerite; quartz, manganosiderite and calcite are gangue minerals; magnetite, pyrite, arsenopyrite, chalcopyrite and tetrahedrite are subordinate. The ore structures are massive, banded, brecciated and crustified; the textures are coarse-crystalline corrosional and of mutual boundaries. Ore-enclosing granites underwent hydrothermal alterations: silicification and sericitization in upper levels, carbonate formation and chloritization in the lower ones. The mineral formation involved four stages: (1) quartz-pyrite; (2) magnetite-manganosiderite; (3) galena-sphalerite; and (4) quartzcalcite. Pro-ductive associations were formed at 320-180 °C and at a pressure of 450-300 kgf/cm^2.

According to I. Zlatogurskaya, a zonality pattern is expressed in high concentrations of lead in the central parts of the upper horizons of the deposit, and in high contents of zinc along the periphery and in the lower horizons.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

Volcanogenic hydrothermal lead and zinc deposits with silver are known in the Soviet Union from Transbaikal region (Novoshirokinskii), Central Asia (Kanimansur, Zambarak, Lashkerek), Transcarpathia (Beregovskii, Beganskii), Transcaucasia (Shaumyan, Mekhman, Gumushkhan), and in other countries such as Bulgaria (Madzharovo), Yugoslavia (Zletovo) and Peru (Kasapalka). Host rocks consist of volcanics (lavas, pyroclastic rocks) of the andesite-dacite and dacite-rhyolite formation, to which the deposits are paragenetically related. Ore is confined to the extrusive and subvolcanic vent facies of the volcanics. The deposits are localized in volcanic structures, synvolcanic shear zones as well as in circular, radial and linear fissures. The ore bodies occur as veins, lenses,
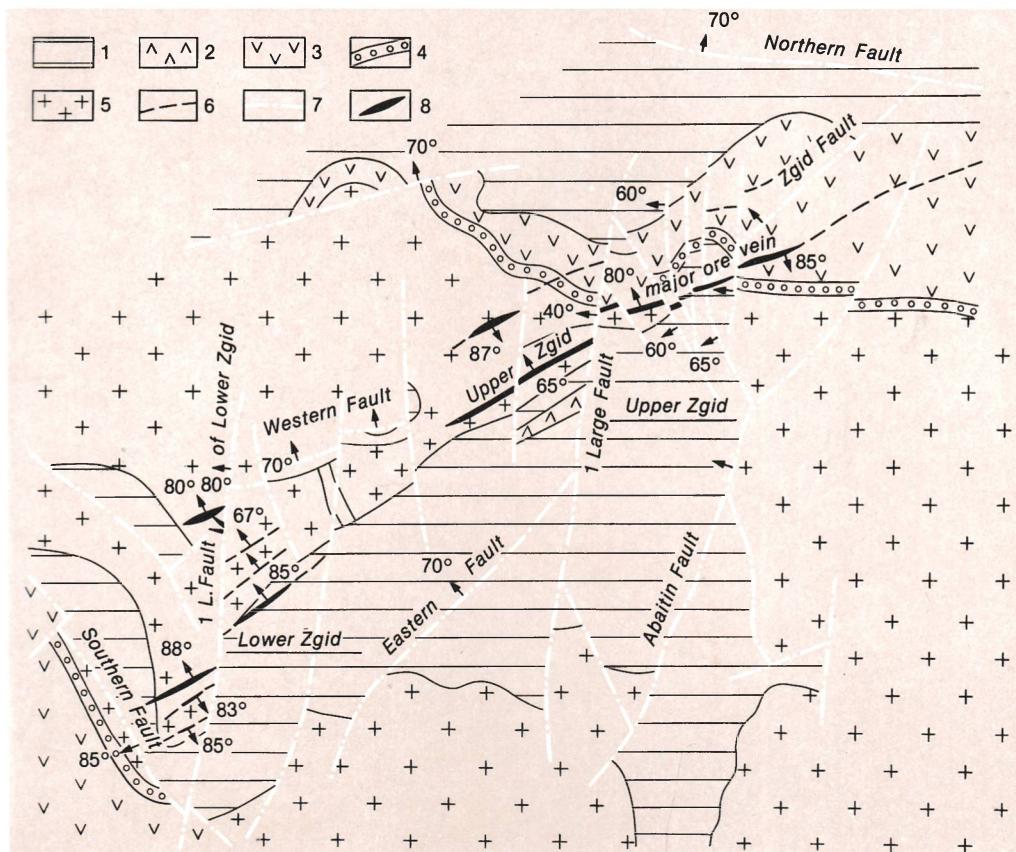
Fig. 59. Schematic geological map of the Zgid deposit. (After V. Sorokin):

1 – shales;
2 – porphyrite dikes;
3 – cover porphyrites;
4 – basal conglomerates;

5 – granites;
6 – ore-enclosing fissures;
7 – pre-ore faults;
8 – ore veins

or, rarely, stockworks. They are traceable for tens or some hundred metres along the strike and dip; the thickness of the ore bodies varies from 0.1 to 1-1.5 m.

Main ore minerals include galena, sphalerite, pyrite and in places, chalcopyrite; gangue minerals are represented by quartz, calcite, less commonly, barite and fluorite; arsenopyrite, grey ore, bornite, pyrargyrite, argentite and boulangerite, as well as siderite, ankerite, dolomite, adular, chalcedony and kaolinite are subordinate minerals. The ore is characterized by the stringer, disseminated, banded, brecciated and crustified structures; the textures are fine- to medium-grained, metacolloidal and colloform. Propylites, secondary quartzites and quartz-hematite metasomatites were

formed during the pre-ore time. Wall-rock alterations consist of silicification, sericitization, carbonatization, less frequently, of chloritization, adularization and kaolinization.

The mineral formation involved several stages: (1) quartz-pyrite-chalcopyrite or quartz-adular-pyrite; (2) quartz-hematite; (3) barite-fluorite-galena-sphalerite; (4) post-ore quartz-carbonate. The ores were deposited at the temperature range of 300-100 °C. The ore zonality manifests itself in a substitution of the pyrite-chalcopyrite association for the chalcopyrite-sphalerite one, and then for the galenite-sphalerite association in a direction from deeper to upper levels of the deposit, and from its central parts to flanks. The ore was formed under subvolcanic environments

with depths varying from a few hundred to 1 000 m, the ore interval being first hundreds of metres.

STRATIFORM DEPOSITS

Lead and zinc stratiform deposits are known in the Soviet Union from Yakutia (Sardana), Kazakhstan (Mirgalimsai, Shalgia) and Central Asia (Uch-Kulach, Sumsar, Jergelan), and abroad in Poland (Olkusz, Boleslav), Bulgaria (Sedmochislenitzy), Yugoslavia (Mezhitza), Austria (Bleiberg), France (Larajatiere, Malin, Trèves), Italy (Raibl), Spain (Reosin), Iran (Anguran), Morocco (Bu-Bekker), Algeria (El Abed), Tunisia (Sidi Drio), the USA (Mississippi-Missouri) and Canada (Pine Point). The deposits are confined to carbonate rocks of the great thickness (dolomites, limestones) mainly dated as the Paleozoic and, less frequently, Mesozoic age. Ore-bearing carbonate formations extend for tens and hundreds of kilometres and are localized in ancient and epi-Hercynian platform sedimentary covers as well as in the upper stages of geosynclinal complexes. The distinguishing feature of the deposits is a strict stratigraphic and lithologic control and the absence in their vicinity of any magmatic complexes with which ore could be associated.

Ores occur mainly as concordant sheet-like and lenticular bodies of a multi-stage structure. Less common are intersecting vein- or pipe-like ore bodies. The ore bodies are generally notable for a great extension along the strike varying from hundreds of metres to a few kilometres and up to 800-1 000 m along the dip. Their width ranges from 0.5 to 200 m, on the average, from 10 to 20 m. The ores are simple in composition consisting of lead-zinc, lead or zinc. Main ore minerals are represented by sphalerite, galena and, locally, pyrite; gangue minerals include calcite, dolomite and rarely barite; marcasite, chalcopyrite, bornite, occasionally lead sulphosalts (gratonite and jordanite) are subordinate minerals; quartz and fluorite are subordinate gangue minerals. Wall-rock alterations are weak and manifest themselves in dolomitization, less frequently, silicification and carbonatization.

The genesis of stratiform lead and zinc deposits is disputable. Some investigators (F. Volfson, A. Druzhinin, E. Zakharov) consider them as having the epigenetic hydrothermal origin, others (V. Domarev, M. Konstantinov, H. Strakhov, G. Grushchik, G. Shneiderkhen) believe in the syngenetic sedimentary, or (V. Lindgren, A. Germanov, A. Perelman) – in the epigenetic infiltration genesis. A hypothesis is introduced on their polygenic and polychronic formation which implies a combination of the features typical of the syngenetic and epigenetic origin (V. Smirnov, G. Shcherba).

MIRGALIMSAI DEPOSIT is located in Kazakhstan. The area is composed of carbonate rocks of the Upper Devonian Famennian stage and Lower Carboniferous Tournaisian stage. The Famennian sequences (600 m thick) represented by an alternation of limestones and dolomites of the massive, banded and lump structure is the most productive. Most of ore bodies are confined to the second banded horizon (varying in thickness from 2-4 to 24-28 m) composed of dolomites, calcareous dolomites and limestones exhibiting a thin-bedded, massive and occasionally lump structure. They contain up to 4-5% organic carbon, 0.77% of soluble bitumen, as well as unsoluble matter of highly metamorphosed kerabitumen. The carbonate sequence forms wide trough-like synclines separated by complex anticlines. The folds are cut by overthrusts and upthrusts.

Ores occur as concordant bed-like bodies extending for a large distance without an appreciable change in lithology (Fig. 60). Three types of ores are recognized: lead, lead-barite and barite. Main ore minerals include pyrite, galena and sphalerite; gangue minerals are represented by dolomite, calcite, barite, ankerite and quartz; subordinate minerals include chalcopyrite, tennantite, tetrahedrite, arsenopyrite, argentite, magnetite, hematite as well as witherite and fluorite. The oxidation zone (down to 50 m and more) is represented by anglezite, smithsonite, calamine, wulfenite, chalcocite, covellite, plumbojarosite, malachite and azurite as well as by opal and gypsum. The ore is characterized by the lit-par-lit,
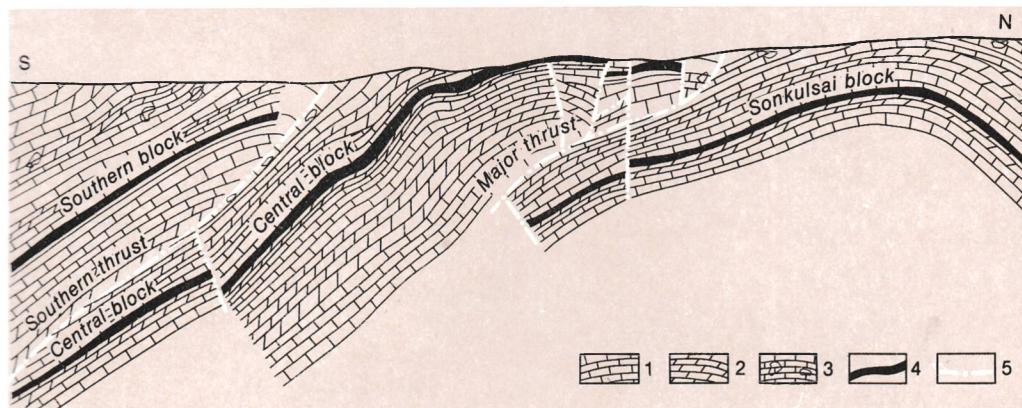
Fig. 60. Scheme showing geological section through the Mirgalimsai deposit (based on the data of Mirgalimsai Geological Prospecting Team):

1 – limestones;
2 – dolomites;
3 – brecciated limestones

4 – ore bodies;
5 – tectonic dislocations

disseminated, banded, stringer, and rarely massive structures; the textures are fine-grained, or of replacement and intersection.

The ore deposition took a long time. According to S. Yushko. it involved three phases: (1) syngenetic, which produced dolomite, quartz, barite, galena. pyrite, sphalerite and chalcopyrite; (2) diagenetic, when dolomite. calcite. galena, pyrite and sphalerite were emplaced; (3) hydrothermal. The hydrothermal phase is subdivided into three stages: (1) ankerite-barite-galena-sphalerite-chalcopyrite; (2) fluorite-calcite-galena-sphalerite; (3) quartz-chalcopyrite.

According to Yu. Bogdanov and M. Golubchina's isotopic data obtained for sulfide sulphur, $\delta^{34}S$ varies from $+28.9$ to -15.2%, which suggests the lateral changes in sulfide-forming conditions in the process of sedimentation. diagenesis and hydrothermal deposition. Biogenic sulphur takes part in the sulfide formation, and bacterial sulphate-reduction also played an appreciable role in their deposition.

MISSISSIPPI-MISSOURI GROUP of stratiform deposits of lead and zinc is situated in the Mississippi River Valley, the USA. Since 1720, a total of 12 million tons of lead and 11 million tons of zinc have been recovered from these deposits. The largest deposits are concentrated in the south-eastern part of Missouri (Fig. 61). Precambrian schists and gneisses are exposed being overlain by

Cambrian and Ordovician sedimentary strata which contain dolomite beds. They form a dome whose core consists of Precambrian granite and volcanics intruded by magmatic bodies and dikes of the basic composition. Ore is mainly confined to thin-bedded dolomites among which a series of beds are recognized. The complex structural pattern of the dolomite unit is due to pinching out, reefs, erosion unconformities, stylolite seams, submarine landslides and to gravitational breccias which are responsible for intricate contours of the ore bodies. Common are thrust and shear faults of the north-western strike, and joints to which individual carbonate-sulphide veinlets are confined.

Ores occur mainly as concordant bodies of the sheet-, lens-, and ribbon-like shapes, as well as rare cross-cutting bodies of the vein and more complex shapes. Some of the bodies are 3-4.5 m wide and extend for 200-500 m along the strike.

Main ore minerals are represented by galena; dolomite is a gangue mineral; subordinate minerals include sphalerite, chalcopyrite, chalcocite, enargite, millerite, pyrite, marcasite, locally siegenite and bravoite as well as calcite, barite, dickite, illite and quartz. The ore is characterized by banded, disseminated, stringer, brecciated, rarely massive and drusy; its textures are fine-grained (rarely coarse-gained), corro-
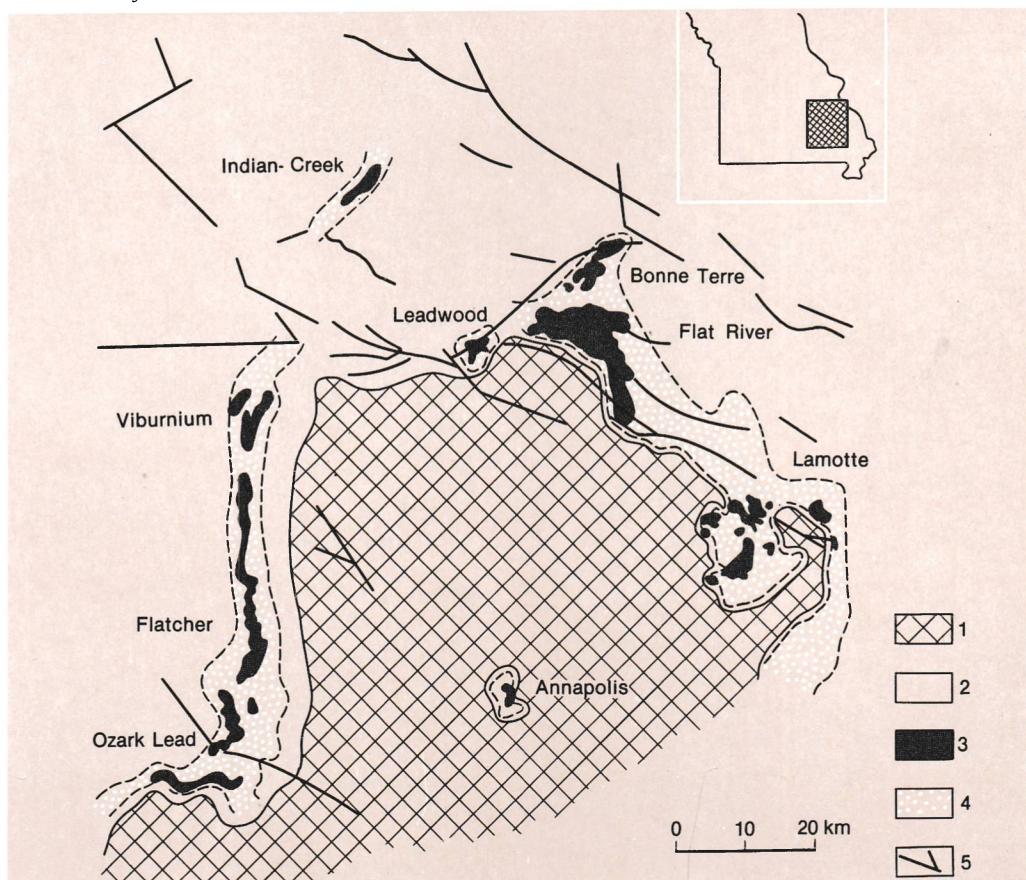
Fig. 61. Stratiform deposits in South-East Missouri. (After G. Kisvarsani)

1 – Precambrian magmatic rocks;
2 – sedimentary rocks of Cambrian and Ordovician;
3 – segments of high-grade ore;

4 – segments of low-grade ore;
5 – major faults

sion, of dilution, zonal, colloform. Ore alterations are obscure and manifest themselves in diagenetic dolomitization and silicification of host rocks. Lead-zink ores compose the central parts of ore-bearing areas, while lead ores occupy the periphery.

Isotopic studies have established the following: (1) lead in galenites is enriched with radiogenic isotopes; (2) $\delta^{34}S$ values vary widely: from $+36$ to -10% for South-Eastern Missouri, and from $+6.3$ to 32.2% for the Upper Mississippi; (3) $\delta^{18}O$ and $\delta^{13}O$ values for limestones and dolomites suggest a very negligible isotopic exchange between rocks and ore-forming fluids in the halos adjacent to ore bodies.

Four hypotheses have been introduced concerning the origin of lead and zinc stratiform deposits: (1) sedimentary hypothesis, according to which these deposits represent primary sedimentary syngenetic deposits which have undergone diagenetic, katagenetic and metomorphic transformations; (2) plutonogenic hydrothermal hypothesis which suggests that these deposits are related to deep-seated hypothetic magmatic rocks; (3) infiltration, or hydatogenic hypothesis, according to which stratiform deposits are epigenetic and are formed under the action of chemically active buried or meteoritic waters of deep circulation; (3) a hypothesis that suggests polygenic and polychronic origin of the deposits under review and introduces the syngenetic and subsequent epigenetic stages of their long-time formation (V. Smirnov).

MASSIVE SULFIDE DEPOSITS

Massive sulfide deposits are known in the Soviet Union in the Northern Baikal region (Kholodninsk), Transbaikal region (Ozernyi), Mountainous Altai (Zyryanovsk, Ridder-Sokolnyi, Tishinskii, Belousovskii), Kazakhstan (Zhairem, Tekeli), Central Asia (Khandiza), the Caucasus (Filizchai, Madneuli), and in other countries such as FRG (Rammelsberg), Spain (Rio-Tinto), Norway (Bleakvassly), Sweden (Falun), Turkey (Ergani), Cuba (Santa-Lucia), the USA (West-Shasta), Canada (Sullivan), Japan (Shakanai), Burma (Boudwin) and Australia (Nairni). They are spatially and genetically associated with acid differentiates of basaltoid volcanism of early eugeosynclinal stages, and are confined to volcanic-dome (stratovolcanoes), vent structures and volcanotectonic as well as caldera-like and intervolcanic depressions, synvolcanic joint zones, and to linear and ring faults.

Usually ores occur as concordant sheets and lenses; veins and stockworks are observed in the hanging wall of these bodies. The upper boundary (hanging wall) of concordant bodies is sharp, occasionally is higher than ore-clasts and the lower boundary (footwall) has a more complicated morphology with steeply dipping apophyses and stringer-disseminated ores which occur among hydrothermal metasomatites. The sheet and sheet-like bodies extend for hundreds of metres (locally up to 1-2 km) along the strike and 500-600 m and more along the dip, their thickness attaining 15-20 m, in places, 50 m.

In terms of composition the ores are copper-lead-zinc and lead-zinc, rarely, lead. Pyrite is the predominant mineral accounting for 80-90% of the metallic minerals; the main minerals also include sphalerite, galena and, occasionally, chalcopyrite; gangue minerals are represented by quartz and barite. Pyrrhotite, arsenopyrite, grey ores, bournonite and marcasite as well as calcite, dolomite, chlorite and sericite are subordinate. Wall-rock metasomatites consist of quartz-sericite-chlorite, quartz-sericite, quartz-microcline, quartz-carbonate, beresite-listvenite and quartz rocks. The halo of altered rocks is sharply assymmetric, the

rocks occur predominantly in the foot-wall of the bodies.

The formation of ore mineralization took a long time and involved 2-3 phases. (1) syngenetic volcanogenic-sedimentary (200-100 °C); (2) epigenetic hydrothermal-metasomatic phase that included several stages: (a) quartz-pyrite (360-330 °C); (b) sphalerite-galena (320-280 °C); (c) barite-galena (280-230 °C); (d) quartz-carbonate (260-180 °C); (3) metamorphic-hydrothermal, or regeneration stage, which involved recrystallization and redeposition of ores under the influence of late metamorphic, magmatic and hydrothermal processes. Zonality manifests itself in that massive sulfide ores of iron pyrite, copper-pyrite, copper-zinc, polymetallic and barite-polymetallic compositions successively replace each other starting from the lower and central parts of deposits towards upper horizons and flanks.

Two ore formations are recognized in massive sulfide deposits of lead and zinc: (1) chalcopyrite-galena-sphalerite-pyrite in volcanogenic complexes (Zyryanovsk, Ridder-Sokolnyi in the USSR; Rio Tinto in Spain; Shakanai in Japan); (2) galena-sphalerite-pyrite, in volcanogenic-terrigenous and volcanogenic-carbonate complexes (Filizchai, Zhairem in the USSR, Rammelsberg in FRG).

Deposits of Chalcopyrite-galena-sphalerite-pyrite Formation in Volcanogenic Complexes

RIDDER-SOKOLNYI DEPOSIT is situated in Mountainous Altai. It was discovered in 1784 and has been exploited ever since. The area is composed of Lower Paleozoic metamorphic schists and predominantly Eifelian volcanogenic-sedimentary rocks (over 2000 m in thickness). The succession of the latter is represented (from bottom to top) by: (1) lava, lavobreccia and tuff of rhyolitic composition; (2) aleuropelite, microquartzite, calcareous shales and chert; (3) lavas and tuffs of andesite-basalt composition; (4) argillite and aleurolite covered with basalt sheets and sheet-like bodies of rhyolite porphyries of effusive, extrusive and subvolcanic facies. Pre-Middle Devonian, Devonian and Upper Paleozoic
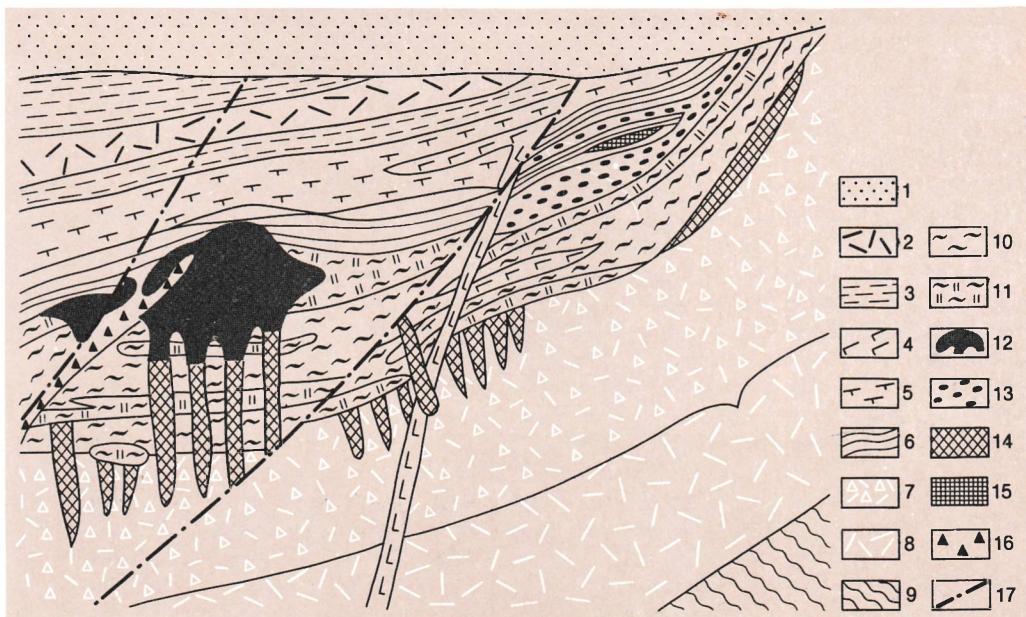
Fig. 62. Combined geological section through the Ridder-Sokolnyi deposit, Mountainous Altai. (After B. Cheprasov, I. Pokrovskii, O. Kovrigo):

1 – Quaternary sediments;
2-6 – Middle Devonian basalt-liparite formation:
  2 – subvolcanic and extrusive porphyries;
  3 – limy aleurolites of the Sokolnyi formation;
  4 – subvolcanic andesite-basaltic porphyries;
  5 – basic tuffs and tuffites of the Ilyin formation;
  6 – aleurolites of the Kryukov formation;
7-8 – Leninogorsk formation:
  7 – agglomerate acid tuffs;
  8 – lava of liparite porphyries;
9 – Ordovician metamorphic rocks;
10-11 – wall-rock metasomatites:
  10 – microquartzites and sericite microquartzites;
  11 – sericite-chlorite-quartz metasomatites;
12-15 – ores:
  12 – barite-polymetallic;
  13 – disseminated polymetallic;
  14 – copper-zinc;
  15 – polymetallic massive and banded;
  16 – late ore eruptive breccias;
  17 – faults

granitoids are developed in the area; veined magmatic derivatives are represented by post-ore diabase dikes.

Gently-folded Eifelian volcanogenic-sedimentary rocks compose an intervolcanic depression. In its northern part there is the Early Eifelian Ridder-Sokolnyi paleovolcano stretched along restricting sublongitudinal synvolcanic faults which serve as ore-feeding channels. On the southern slope of the paleovolcano buried under tuffaceous sedimentary rocks and basic volcanic rocks dome-like structures are developed. Mineralization localized in acid tuffs is confined to these structures.

Ores occur as sheets and lenses with veins and stockworks being in their footwalls (Fig. 62). The vertical thickness of the mineralization exceeds 600 m.

Predominant among massive sulfide ores are lead-zinc (Pb : Cu : Zn = 1 : 2.1 : 0.2) and copper-zink (Pb : Cu : Zn = 1 : 4.3 : 8.1) ones. Main ore minerals include sphalerite, pyrite, galena, chalcopyrite; gangue minerals are represented by quartz, calcite, hydromica, phengite, dolomite and barite; tetrahedrite, marcasite, arsenopyrite and silver as well as chlorite, epidote, albite, ankerite, kaolinite, magnesite, siderite and chalcedony are subordinate. The ore is characterized by massive, banded, stratified, disseminated and stringer structures, and by hypidiomorphogranular, subgraphical and metacolloidal textures.

In the footwall of the ore bodies hydrothermal-sedimentary microquartzite and dolomite rock as well as hydrothermal metasomatites (chlorite microquartzite, sericite-dolomite and quartz-barite rocks) are developed.

According to I. Pokrovskaya and O. Kovrigo, the formation of ore mineralization took a long time and involved three phases:
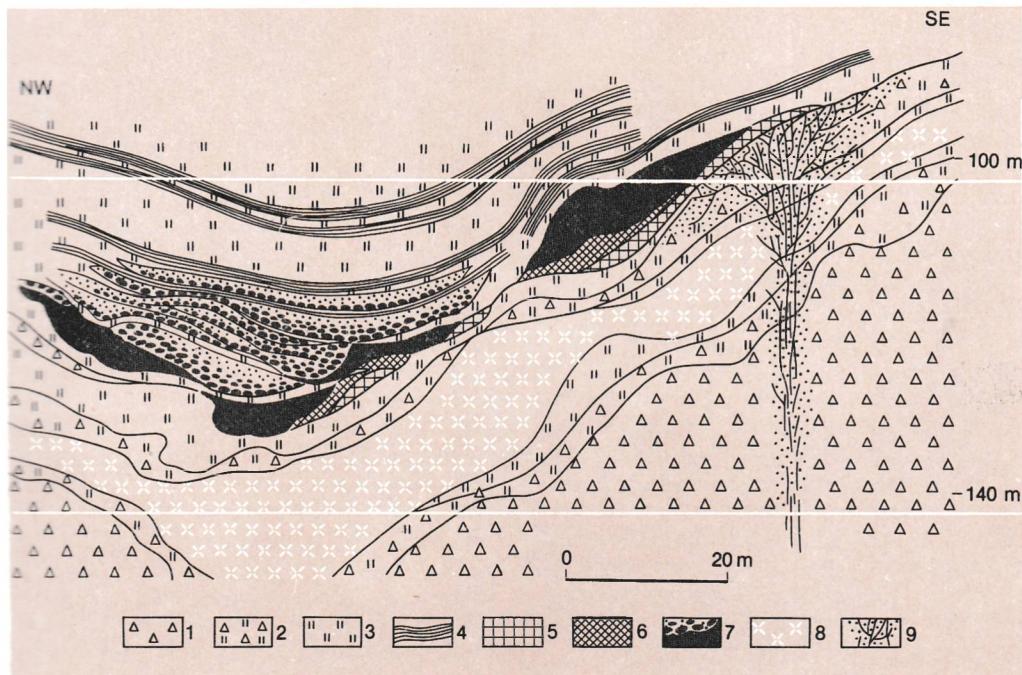
Fig. 63. Geological section through the Shakanai deposit. (After I. Kadzirava):

1 – olcanic rhyolite breccias;
2 – tuff-breccias;
3 – tuffs and lapilli tuffs;
4 – argilites;

5 – pyrite ore;   6 – yellow ore;
7 – black ore;
8 – gypsum;
9 – sulfide stringers

hydrothermal-sedimentogenetic (under C), which produced bedded massive sulfide polymetallic ores (Second Ridder ore occurrence); (2) hydrothermal-metasomatic 345-125 C), in which the main mass of the Ridder-Sokolnyi ores was deposited; (3) hydrothermal-metamorphogenic. According to I. Isakovich and N. Gibshner, formation of ore mineralization in the second phase can be subdivided into four stages: (1) pre-ore pyrite; (2) galena-chalcopyrite-sphalerite (325-125 C); (3) galena-sphalerite 345-145 C); (4) post-ore quartz-carbonate. Vertical zonality manifests itself in the occurrence of copper-zinc ores at deep horizons, the lead-zinc ore at intermediate ones, and barite-polymetallic at the upper horizons.

According to L. Shilov, the isotopic composition of lead in galena suggests the same lead source both for ores and for host rocks. The study of the sulphur isotopes by A. Avdonina, L. Grinenko and D. Voinkova indicates that the sulphur has a deep-seated homogenic source.

SHAKANAI DEPOSIT is located in Japan. It is a typical "kuroko" type deposit. The area is composed of Miocene sediments and volcanic rocks which are subdivided into two formations: the Shakanai formation at the base and Saynokami one at the top. Two members are distinguished in the Shakanai formation (500 m-thickness): the lower member composed of lavobreccia and rhyolite tuff, and the upper one (ore-enclosing) of banded pumice tuffs, breccias and extrusive rocks of the rhyolite composition. They are overlain by shales forming 10-30 m-thick beds, and by pumice acid tuffs of the Saynokami formation. Subvolcanic rhyolite bodies and diorite dikes are also observed here. Volcanic structure of the area showing generally a gentle dip is manifested by extrusive domes and by local depressions lying between them in which ore bodies most commonly occur (Fig. 63). The structures are complicated by

synvolcanic faults and joint zones which served as ore-feeding channels.

Ores occur chiefly as concordant sheets and lenses, with veins and stockworks at the footwall. The lens-like bodies, in plan, are tens to hundreds of metres long, and 10 to 70 m wide. There are several ore types: "kuroko" (black ore) represented by pyrite-chalcopyrite-galena-sphalerite ore, "oko" (yellow ore) – pyrite-chalcopyrite ore, "ruko-ko" – pyrite ore and "keiko" – represented by siliceous ore with sulfide veinlets. The first three types of ore are considered to be syngenetic, and the fourth type – epigenetic. Main ore minerals include pyrite, chalcopyrite, sphalerite, galena and tetrahedrite; quartz, barite and gypsum are gangue minerals; bornite, hematite, argentite and electrum are subordinate. The ore is distinguished by massive, banded, stratified, brecciated, stringer and disseminated structures; the textures are metacolloidal, colloform, globular, allotriomorphic-granular, emulsion, lattice, interstitial and radially fibrous. Wall-rock alterations are exhibited in argillization, zeolitization, silicification, sericitization and chloritization of the enclosing volcanic rocks.

A distinct vertical zonality is manifested in distribution of various ore types in the ore bodies. Their upper parts are composed of massive black ores. Downward they grade into yellow ores. Then they are replaced by pyrite ores which are represented in the upper part by breccia varieties, and in the lower part by dust-like pyrite, finely dispersed in quartz-sericite metasomatites. At the lower horizons of the ore bodies stockworks of veinlet siliceous ores containing chalcopyrite, sphalerite and galena as well as barite are developed. They are underlain by a gypsum zone with anhydrite that is traceable in the margins of rhyolite extrusives and in pyroclastic rocks.

A temperature zonality manifests itself in formation of siliceous ores of hydrothermal origin at 295-200 °C (215 °C on average), black ores, at 150-70 °C (115 °C on average). Thus, the temperature of ore-bearing fluids decreased to the extent of their movement from the deeper parts, where they deposited ore minerals upward, where they flew out onto the sea floor.

The ore deposition took place in Middle Miocene (13 m.y.), at the epoch of culmination of the submarine volcanic activity which had begun in the Early Miocene and evolved from andesites to rhyolites.

Deposits of Galena-sphalerite-pyrite Formation in Volcanogenic-terrigenous and Volcanogenic-carbonate Complexes

ZHAIREM DEPOSIT is located in Kazakhstan. The area is composed of volcanogenic-sedimentary rocks of the Middle Devonian-Frasnian age, carbonate, argillaceous-carbonate and sandy-clayey rocks of Famennian and Lower Carboniferous. A productive unit composed of coaly-clayey-siliceous-carbonate rocks is attributed to the Upper Famennian substage. Magmatic rocks are represented by a subvolcanic body of trachyte porphyry and dikes of amygdaloidal porphyry. The Famennian and Lower Tournaisian rocks form the Zhairem brachyanticline cut by steep transverse fault and by more gentle interformational detachments (Fig. 64).

Ores occur as concordant sheets and lenses varying in thickness from 5 to 25 m. Syngenetic ores of an iron, iron-manganese and zinc (pyrite-sphalerite) composition and epigenetic ores of a zinc-barite, lead-barite, lead-zinc-barite and barite composition are distinguished. Main ore minerals include pyrite, sphalerite, galena, chalcopyrite, hematite and marcasite; vein minerals are represented by quartz, barite, calcite and dolomite; grey ores, bournonite, millerite, bravoite, jamesonite and boulangerite as well as albite, fluorite, K-feldspar and sericite are subordinate. The ore is characterized by bedded, disseminated, banded and brecciated structures; the textures are globular, colloform, zonal, cement-like, crystalline-granular, corrosional, subgraphical, emulsion, interstitial and cataclastic.

Widely spread are intra-ore explosive breccias whose fragments consist of enclosing rocks, lead-zinc and barite ores; the breccia cement is quartz-dolomite-albite. Wall-rock metasomatites are characterized by the pyrite-quartz, barite, siliceous and siliceous-
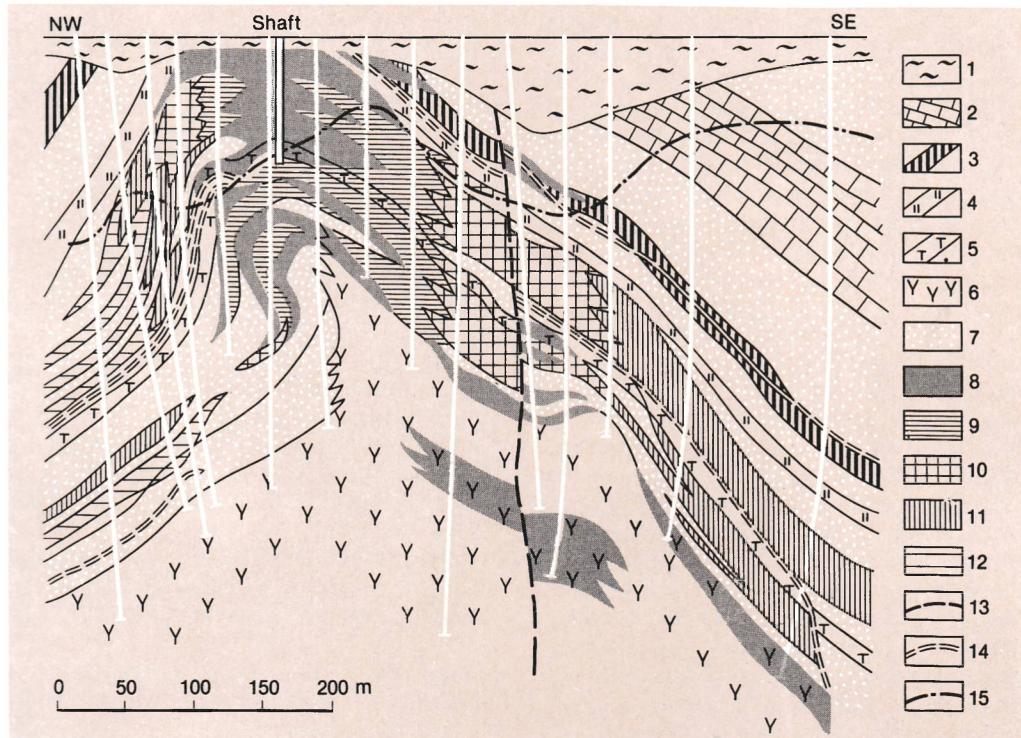
Fig. 64. Geological section through Zhairem deposit. (After A. Rozhnov):

1 – Cenozoic sediments;
2-5 – Famennian rocks:
    2 – red limestone unit;
    3 – layer of banded iron ore;
    4 – bed of carbonaceous-quartz-feldspar rocks;
    5 – layer of tuff-sedimentary rocks;
6 – K-feldspar (trachytic) porphyries;
7 – quartz and quartz-pyrite metasomatites;

8 – barite metasomatites;
9 – lead-barite ore;
10 – barite-lead-zinc ore;
11 – lead-zinc ore with weak baritization;
12 – lead-zinc ore;
13 – faults;
14 – layer-to-layer detachments;
15 – lower boundary of weathering crust

carbonate composition; albitization and silicification, partly dolomitization, sericitization and the chloritization are also too observed.

According to N. Mitryaeva, formation of the Zhairem deposit involved three phases: (1) sedimentary; (2) hydrothermal-metasomatic; (3) late hydrothermal. The first phase is characterized by marine sedimentation and later, by diagenesis accompanied by deposition of sphalerite-pyrite ores (120-100 °C). The second, the main ore phase, involved three stages: (1) the early metasomatic with the albite-dolomite-quartz-sphalerite and pyrite-quartz associations; (2) the major ore metasomatic stage with the sphalerite-galena-barite association (150-140 °C); (3) veinlet stage with the quartz-calcite-fluorite-sulfide association. The third phase of

the ore deposition occurred in two stages: (1) the ore metasomatic stage with the quartz-barite (330-300 °C) and chalcopyrite-barite (280 °C) associations; (2) the stage of late quartz-calcite-barite veinlets (175-170 °C).

The first hydrothermal-sedimentary phase was followed by dislocational metamorphism, recrystallization of ores and redeposition of ore matter. Between the hydrothermal-metasomatic and late hydrothermal phases there was intrusion of subvolcanic bodies of trachyte porphyry and formation of explosive breccias.

According to N. Skripchenko, a horizontal zonality is expressed in formation of the following zones (from the centre towards the periphery): (1) the central zone of quartz, quartz-pyrite and barite metasomatites; (2)

galena-barite metasomatites; (3) galena-sphalerite-barite metasomatites; (4) baritized rich lead-zinc ores; (5) bedded zinc ores. Epigenetic hydrothermal-metasomatic mineralization is typical of the first three zones, it is associated with syngenetic hydrothermal-sedimentary mineralization in the fourth zone, while the last type of mineralization is exclusively developed in the fifth zone.

METAMORPHOSED DEPOSITS

Metamorphosed lead and zinc deposits are known in the Soviet Union within the Yenisei Ridge (Gorevskii, Rossokhin), Northern Baikal region (Tabornyi, Tayeznyi), and in other countries such as Sweden (Laysvaal), the USA (United Verde). Canada (Flin Flon), India (Mokhia-Magra) and Australia (Broken Hill, Mount Aisa, McArthur River). These deposits are confined to Proterozoic and Lower Paleozoic crystalline metamorphic schists as well as to marmorized limestones which compose shields and old folded regions.

Ores occur as concordant sheet and sheet-like bodies of large extension reaching hundreds of metres-a few kilometres along the strike and several hundreds of metres to 1 000 m and more along the dip. The width of the bodies varies from 10 to 100 m. Metamorphic alterations of host rocks are expressed in recrystallization and metamorphism up to the epidote-amphibolite, biotite-garnet, garnet-amphibolite and granulite facies. Hydrothermal alterations are expressed in tourmalization, dolomitization, silicification, sericitization and albitization of host rocks. The ore deposition involved 2-3 phases: (1) primary hydrothermal-metasomatic and hydrothermal-sedimentary; (2) metamorphogenic; (3) regeneration phase. Zonality throughout the thickness of ore bodies is expressed (from the footwall to the hanging wall) in substitution of pyrite-pyrrhotite ores first by pyrite-galena-sphalerite, then by the richest galena-sphalerite ores.

Two ore formations are identified among metamorphogenous deposits: (1) pyrrhotite-pyrite-sphalerite-galena formation in metamorphosed carbonate rocks (Gorevskii in the USSR, Balmat in the USA); (2)

galena-sphalerite-pyrrhotite-pyrite formation in highly metamorphosed silicate sedimentary rocks (Rossokhin in the Yenisei Ridge, Sullivan in Canada, Broken Hill in Australia).

Deposits of Pyrrhotite-pyrite-sphalerite-galena Formation in Metamorphosed Carbonate Rocks

GOREVSKII DEPOSIT is located in the Yenisei Ridge. The area is composed of the Upper Riphean sequence (1 000-1 160 m thick) consisting of rhythmically bedded limestones intercalated with marls which are regionally metamorphosed into quartz-sericite-calcareous and quartz chlorite-calcareous schists. There occur dikes and stocks of olivine dolerite of the Late Riphean complex (915 m. y.).

Precambrian rocks are intensely deformed and broken into blocks. They form an NW-trending asymmetric Gorevskii syncline complicated by minor folds with dips of the limbs varying from 55-80° to vertical. The eastern limb is cut by longitudinal faults accompanied by a milonite and tectonite zone as well as by zones of intensive foliation.

The largest bodies are represented by flattened lenses which lie conformably with the host rocks, and with zones of layer-to-layer foliation (Fig. 65). The ore bodies at the lower horizons have a columnar shape. Main ore-forming minerals are galena, sphalerite and pyrrhotite; gangue minerals are quartz, siderite, ankerite, dolomite and calcite; subordinate minerals are represented by pyrite, marcasite, magnetite, boulangerite, jamesonite, bournonite, arsenopyrite and chalcopyrite as well as chlorite, muscovite, biotite, sericite, grossular, tremolite, epidote, albite, apatite and tourmaline. Oxidation zone contains cerussite, anglesite, pyromorphite and covellite. The ore is characterized by banded, mottled and brecciated as well as disseminated, stringer and massive structures; the main textures are hypidiomorphic and allotriomorphic.

Host rock alterations have resulted in the formation of amphibole-garnet-biotite skarnoids, dolomite-ankerite, siderite and quartz-carbonate rocks, and quartzites.
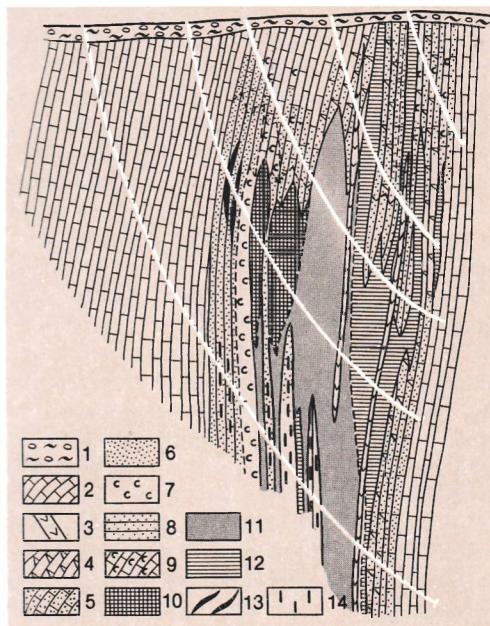
Fig. 65. Schematic geological section through the Gorevskii deposit. (After M. Prosnyakov and R. Volodin):

    1 – loose sediments;
    2 – limestones;
    3 – olivine diabases;
 4-9 – hydrothermally altered rocks:
    4 – dolomitized limestones;
    5 – silicified limestones;
    6 – quartzites;
    7 – siderite;
    8 – quartz-carbonate rock;
    9 – sideritized limestones;
10-14 – types of ore:
   10 – zinc-lead;
   11 – lead-zinc;
   12 – lead;
   13 – galena-sphalerite stringers;
   14 – pyrrhotite ore

The ore deposition involved several phases: (1) pyrrhotite; (2) galena-pyrrhotite-sphalerite; (3) galena-pyrrhotite; (4) galena. According to M. Prosnyakov, R. Volodin and M. Sherman, zonality is expressed in the following: pyrrhotite-galena ores $(Pb:Zn = 1.6:1)$ occur in the footwall of the ore bodies; sphalerite-pyrrhotite-galena $(Pb:Zn = 4.5:1)$ ore constitutes the middle part; and galena-sphalerite-pyrrhotite $(Pb:Zn = 0.72:1)$ ores compose the hanging wall; the lead content increases and that of zinc decreases with depth.

The age of the Gorevskii deposit is Late Precambrian $(870 \pm 100$ m.y.).

Deposits of Galena-sphalerite-pyrrhotite-pyrite Formation in Highly Metamorphosed Sedimentary Rocks

BROKEN HILL DEPOSIT is situated in Australia. Since 1883 it has yielded 120 million tons of ores, the average lead and zinc content being 25%. The total metal reserves of the Broken Hill deposit (plus the ore recovered) are estimated at 55 million tons. The area is composed of the Lower Proterozoic (1 650-1 700 m.y.) sillimanite and andalusite schists, gneiss, metaquartzite and amphibolite. These are cut by intrusive bodies of granite (1 500 m.y.) and ultrabasic rocks, and by pegmatite and dolerite dikes. Early proterozoic rocks form a large syncline complicated by sublongitudinal isoclinal folds and cut by shear zones and faults into separate blocks.

The Broken Hill deposit consists of a series of contiguous subparallel ore bodies traceable for 7 km along the strike and up to 1 000 m to depth. Their thickness is up to 250 m. The maximum thickness of the ore bodies is observed at hinges of festoon folds (Fig. 66). Main ore minerals consist of recrystallized sphalerite (marmatite) and galena; pyrrhotite, chalcopyrite, arseno-pyrite, löllingite and tetrahedrite are subordinate. Most common among gangue minerals are garnet (spessartite), rhodonite and bustamite; less common, feldspar, hedenbergite, ilvaite, wollastonite, apatite, gahnite, damurite, fluorite, quartz and carbonates. The pre-Paleogene oxidation zone represented by a gossan (Pb 10-25%, Ag 60-900 ppm) extends to a depth of 100-200 m. The ore is characterized by plicated, banded and stringer structures, the textures are coarse-grained, recrystallized and granoblastic.

Three stages of the ore deposition are identified: (1) primary volcanogenic-sedimentary; (2) metamorphogenic; (3) regeneration stage. Late hydrothermal veinlets with rare silver sulfides derived from old ores formed at regeneration stage.

Vertical zonality manifests itself in occurrence of zinc ores above lead ores. Horizontal zonality is expressed in the development of zinc ores in the south-west and the lead ores – in the north-east. The
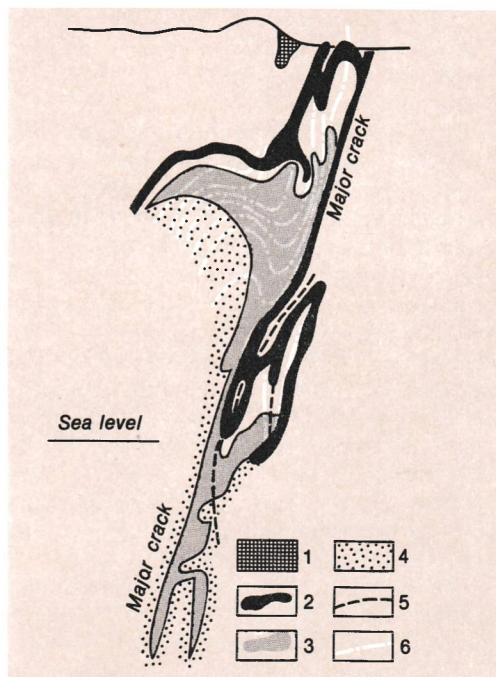
Fig. 66. Schematic geological section through the Broken Hill deposit. (After I. Johnson and G. Klinger):

    1 – upper layer of zinc ore bodies (No. 1);
    2 – middle ore body (No. 2);
    3 – lower ore body (No. 3);
    4 – disseminated ore;
    5 – axes of the second order synclines;
    6 – axes of the second order anticlines

Broken Hill deposit was previously considered to be of hydrothermal origin, at present, however, most of the Australian geologists attribute it to a stratiform primary volcanogenic-sedimentary deposit, which was subsequently intensively metamorphosed together with the host rocks to the granulite facies.

12 TIN DEPOSITS

Tin in alloys with copper was responsible for appearance of the "Bronze Century" (4 000-1 000 years B.C.) in the history of the mankind. In ancient times tin was mined on the territories of the present-day England, Bolivia, China and the USSR (Kalba). Tin has been extensively used due to its fusability, softness, malleability, chemical resistance and ability of producing high-

quality alloys. Tin is used for production of white tin-plate and foil. The main spheres of its application are food industry (40%), aviation, automobile, shipbuilding and radiotechnical industries as well as printing business, dying production, galvanoplastics, glass and textile industries. Tin is recovered from tin, tin-tungsten, tin-silver and tin-polymetallic ores.

The price of one ton of tin is 6 870 US dollars. In 1975 the developed and developing countries produced 170 200 tons of tin concentrate; tin reserves were estimated as follows: 3 million tons of prospected, 6.8 million tons of total reserves. Unique primary tin deposits (Kinta in Malaysia, Mount Pleasant in Canada) have over 100 000 tons of reserves, large deposits possess 100 000-25 000 tons, medium deposits – 25 000-5 000 tons, and small deposits contain under 5 000 tons of tin reserves. High-grade ores contain over 1% tin, ordinary ores – from 1 to 0.4%, low-grade ores – from 0.4 to 0.1%. Placer deposits are mined at 0.01 to 0.02% or 100-200 g/m^3 of tin, though there are high-grade placer deposits with 2 to 3 kg/m^3 tin.

GEOCHEMISTRY AND MINERALOGY

Tin has 10 isotopes with mass numbers of 112, 114-120, 122 and 124, the predominant among them being ^{116}Sn (14.24%), ^{118}Sn (24.01%) and ^{120}Sn (32.97%). Tin is an element of dual geochemical nature predominantly lithophyle and partly chalcophile, depending on oxygen and sulphur regime; with a deficiency of oxygen at late hydrothermal stages, tin and sulphur compose sulphostannates. Crustal abundance (clarke) of tin is $2.5 \cdot 10^{-4}\%$. Its content is low in ultrabasic ($5 \cdot 10^{-5}\%$) and basic ($1.5 \cdot 10^{-4}\%$) rocks and high in acid magmatic rocks ($3 \cdot 10^{-4}\%$). Tin concentration coefficient is 2 000.

Endogenous commercial tin concentrations are associated with acid and moderately acid igneous rocks – granites and granodiorites as well as with rhyolites. Tin is transported by postmagmatic fluids with a rather high content of volatiles (F, B). It is present in ore-bearing fluids in the form of

complex fluorine compounds, and according to V. Barsukov, as a hydroxofluorinestanna-te ion $[Sn(OH, F)_6]$ in an alkaline solution. A decrease of the pH value to 7-7.5 causes a hydrolysis of this complex resulting in formation of hydrofluoric acid and in precipitation of tin hydroxide which, as a result of dehydration, is transformed into water-free dioxide (cassiterite).

Cassiterite is stable in exogenous conditions and accumulates in placers; tin sulphostannates are oxidized and replaced by colloform cassiterite. As it is shown by the analysis of fluid inclusions (A. Kokorin and D. Kokorina), tin deposits are formed at a temperature range of 550-50 °C, with a pressure change from 1 500 to 30-50 kgf/cm^2 from complex hydrothermal solutions (Na and Ca cations and Cl, F, HCO_3 and SO_4 anions being predominant) of a variable concentration from 2-3 to 60 weight percent.

A total of 20 tin minerals are known. Of commercial importance is cassiterite SnO_2 (78.6%) (main tin ore mineral), as well as stannine Cu_2FeSnS_4 (27.7%), tillite $PbSnS_2$ (30.4%), frankeite $Pb_5Sn_3Sb_2S_{11}$ (17%) and cylindrite $Pb_3Sn_4Sb_2S_{14}$ (26%).

METALLOGENY

Tin endogenous deposits belong to postmagmatic formations of the acid and moderately acid magma. They were formed at the middle and mainly at the late stage of a geosynclinal cycle and also in relation to tectono-magmatic reactivation of platforms and regions which have been already folded. Pegmatite and greisen deposits are associated with alaskite granite, skarn and plutonogenic hydrothermal deposits – with granitoids of the relatively high basicity, and volcanogenic hydrothermal deposits are related to acid volcanics (rhyolites, dacites). Tin-bearing granitoids and associated deposits are confined to orogenic zones, median massifs and to volcanic belts; they are controlled by major faults, and appear to be localized frequently at the points of intersection of positive folded structures. A suggestion has been made by L. Baumann

indicating that cassiterite stratiform deposits in metamorphosed volcanogenic-sedimentary rocks of Upper Proterozoic-Lower Paleozoic in the Ore Mountains in GDR belong to volcanogenic-sedimentary type of the early stage of the geosynclinal cycle. Exogenous placer deposits were formed during a platform cycle, in continental or coastal-marine conditions.

Tin deposits were formed in different geological epochs of the Earth evolution, their number and reserves increasing from older to younger epochs. The Archean and Proterozoic epochs produced pegmatite, greisen and skarn deposits (Kitelya in Karelia, Manono-Kitotolo in Zair). The Caledonian deposits of the same type (Mount Cliveland in Australia) are also known. Much more common are greisen, skarn and plutonogenic hydrothermal deposits of the Hercynian epoch (Baimurza in Kazakhstan; Uchkoshkon in Central Asia; Altenburg in GDR; Čynovets in Czechoslovakia; Dollcoats in Great Britain). But the richest plutonogenic and volcanogenic hydrothermal tin deposits are attributed to the Kimmerian and Alpine epochs (Valkumei in Chukotka, Deputatskii in Yakutia, Solnechnyi in Amur river region, Khrustalnyi in Primorski Krai, Khapcheranga in Transbaikal region; Llallagua and Potosi in Bolivia; Lost River in the USA; Akenobe in Japan). The richest tin placers were formed during the Alpine and Recent epochs in the South-Eastern Asia (Malaysia. Indonesia, China).

TYPES OF COMMERCIAL DEPOSITS

Tin commercial deposits are subdivided into: (1) pegmatite; (2) skarn; (3) greisen; (4) plutonogenic hydrothermal; (5) volcanogenic hydrothermal; (6) placer.

PEGMATITE DEPOSITS

Tin pegmatite deposits are known in the Soviet Union in Eastern Siberia, in other countries – in Zair (Manono-Kitotolo), the USA (Silver Hill), Canada (Bird River). The deposits are localized along margins of biotite and bi-mica granite massifs or in their exocontact zone at a distance of

2-3 km. They are mostly localized in the Precambrian complexes, less frequently, in geoanticlinal zones of the folded regions of caledonides and hercynides. The tincontaining pegmatites compose veined, stock- and lens-like bodies. Pegmatite bodies form extended (up to 10-15 km) fields whose width attains a few hundred of metres.

Usually, the ores are complex, and are exploited for Sn, Ta, Nb, Sc, Li and Rb, partly for W and Bi. Albite and albitespodumene pegmatites show the highest tin content (up to 0.1%) which is related to superimposed later processes of albitization and greisenization. Main ore minerals include cassiterite, spodumene, petalite, ambligonite; gangue minerals are represented by quartz, microcline and albite as well as topaz and tourmaline; tantalite and wolframite are rare. Cassiterite is represented by dispersed disseminations up to 0.1-2 cm in size, commonly by large bipyramidal crystals of black colour; Ta, Nb, Zr and Sc are typomorphic admixtures.

The tin-bearing pegmatites have no practical importance but are a valuable source of cassiterite placers.

GREISEN DEPOSITS

Tin greisen deposits are known in the Soviet Union in Chukotka (Ekug), Yakutia (Kester, Butygychag), Transbaikal region (Etyka), Primorski Krai (Chapayevskii), Maly Khingan (Olonoisk) and Central Asia (Aktas); in other countries they are known in GDR (Altenberg), Czechoslovakia (Cynovets), the USA (Lost River in Alaska), China (Limu), Burma (Maucha). They are associated with leucocratic alaskite granite intrusions of a hypabyssal facies, and are confined to their cupolas, stocks and apophyses. The deposits are localized both in granites and in their cover rocks. They are often associated with greisen deposits of other metals, especially those of tungsten. Their age varies from Archean to Alpine, inclusively. But they are most typical of Hercynian and Kimmerian metallogenic epochs. The deposits are formed at the middle and late stages of the geosynclinal cycle as well as during platform reactivation.

Tin greisen deposits are chiefly represented by veins localized in shear zones and by stockworks associated with minor jointing which is usually related to prototectonics. Less commonly the ores appear as pipe-like bodies confined to the intersection of fissures or faults. Individual veins extend for tens to hundreds of metres along the strike and along the dip, their thickness varying from 0.1 to 2-3 m, usually 0.5-1 m. The veins form fields that extend for a few kilometres along the strike and up to 1 000-1 200 m along the dip.

The ores are usually complex and apart from Sn contain W, Li, Ta and Nb. Main ore minerals are cassiterite, wolframite, arsenopyrite, zinnwaldite; gangue minerals include quartz, albite, orthoclase, muscovite, siderophyllite, topaz, fluorite, tourmaline; pyrrhotite, bismuthite, magnetite, scheelite, chalcopyrite, sphalerite, galena, hematite as well as adularia, sericite and calcite are subordinate. Host rocks are subject to greisenization, K-feldspathization and albitization.

The ore deposition involved several phases: (1) the pre-ore microcline-albite phase; (2) quartz-cassiterite phase accompanied by formation of greisens; (3) cassiterite-wolframite phase; (4) sulfide phase, locally with cassiterite; (5) quartzcarbonate-fluorite phase. Tin greisen deposits are formed from the highly concentrated, multi-component hydrothermal solutions at a temperature interval of 500-200 °C.

Horizontal zonality is characterized by a decrease in a cassiterite content and by an increase in a sulfide content as one moves away from the intrusion. A similar situation is observed along the ascending ore veins. A reverse vertical zonality is also occasionally observed; for example, according to I. Drabkin, at the upper levels of the Butygychag Deposit (Yakutia), the cassiterite content of ores decreases with depth, cassiterite being substituted by sulfides.

Greisen deposits belong to cassiteritequarzt formation identified by S. Smirnov.

ETYKA DEPOSIT is located in Transbaikal region. The area is composed of a sandy shale sequence of Lower-Middle Jurassic

which is crumpled into folds and complicated by a fissure zone. Two intrusive complexes of the Kimmerian age have been established: (1) granodiorite complex with dikes of plagiogranite-porphyry, granite-porphyry and diorite porphyrite; granite complex composed of early biotite and of late amazonite granite.

Ores are represented by topaz-quartz veins localized in gently dipping fissures of detachment, and by more persistent quartz-amazonite veins in steep joints trending from north to south (Fig. 67). Main ore minerals are cassiterite and zinnwaldite; gangue minerals include quartz, topaz (or amazonite) and K-feldspar; stannite, wolframite, arsenopyrite, chalcopyrite, sphalerite and galena as well as albite, fluorite are subordinate. Ore is characterized by massive, blocky, brecciated, banded and veined structures; textures are crystalline and colloform.

The ore deposition involved three stages: (1) quartz-topaz I or quartz-amazonite; (2) quartz-topaz II, or zinnwaldite-fluorite (350-290 °C); (3) albite-orthoclase with sulfides (230-150 °C). Cassiterite was mainly emplaced in the first and partially in the second stage, the amount of sulfides tends to increase by the beginning of the last stage.

ALTENBURG DEPOSIT is located in the GDR and is confined to the cupola of the Hercynian Altenburg granite-porphyry stock which has intruded the quartz porphyry. The ore body represents a pipe-like stockwork, 0.4 × 0.5 km across. It was formed in the granite-porphyries which were pierced by a set of minute prototectonic fissures (Fig. 68). Greisens consist of quartz (60%), mica (30-35%) and topaz (5-7%). Main ore-forming minerals are zinnwaldite and cassiterite; bismuthine, native bismuth, arsenopyrite, pyrite, chalcopyrite, molybdenite, wolframite, hematite, magnetite, sphalerite and grey ores are subordinate. Gangue minerals are quartz, topaz (main); fluorite and siderite are subordinate. Granite-porphyry is intensely greisenized.

The following phases of ore deposition are distinguished: (1) K-feldspar; (2) albite; (3) quartz-zinnwaldite-topaz with cassiterite and wolframite; (4) late K-feldspar; (5) fluorite-
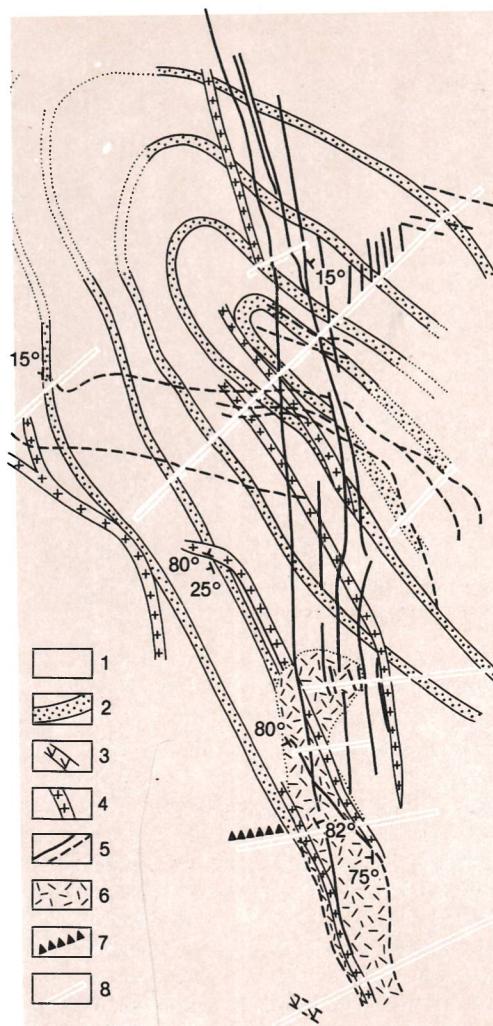
Fig. 67. Scheme showing the structure of the second sector of the Etyka tin deposit. (After O. Levitskii, V. Aristov, R. Konstantinov, E. Stankeev):

1 – sandstones, aleurolites, shales;
2 – gravelly conglomerates;
3 – dikes of pre-granitic diorite-porphyries;
4 – dikes of plagiogranite-porphyries;
5 – ore veins:
a – quartz-amazonite;
b – topaz-quartz;
6 – greisenized rocks;
7 – brecciation zone;
8 – trenches

sulfide with hematite. The central zone of the deposit is composed of rich ores, the peripheral portions are less rich in tin and have a high sulfide content (arsenopyrite is predominant).

9 – 824
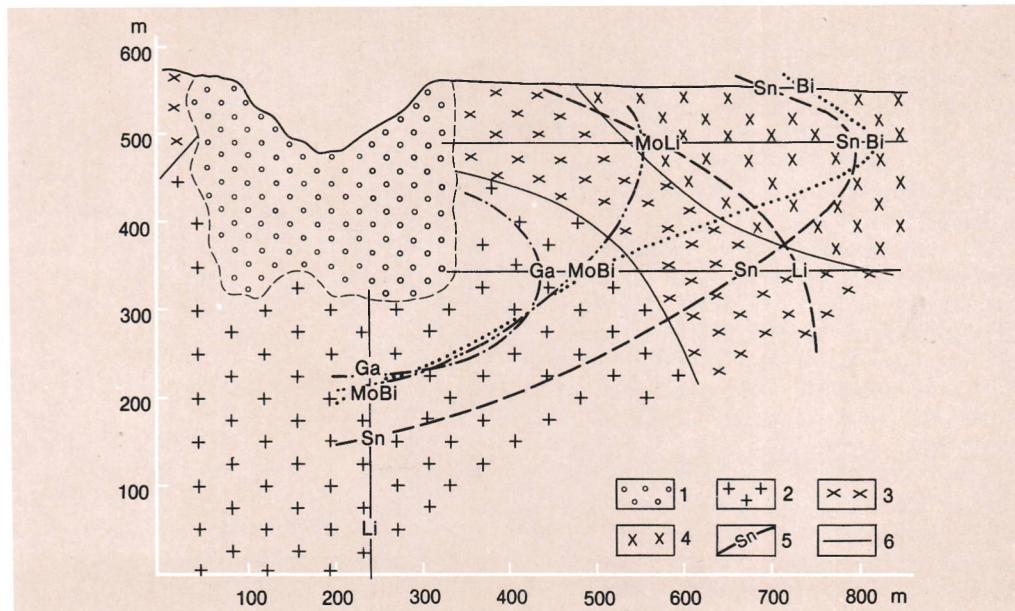
Fig. 68. Scheme showing the structure of the Altenburg greisen deposit wihh endogenous geochemical halos. (After G. Iischendorff):

1 – tin-bearing greisen stock;
2 – granites;
3 – granite-porphyries;

4 – quartz-porphyries;
5 – anomalous content of tin;
6 – lines of geochemical profiles

SKARN DEPOSITS

Tin skarn deposits are known in the Soviet Union in Primorski Krai (Yaroslavl'), Central Asia (Maikhura, Sary-Bulak) and Karelia (Pitkyaranta, Kitelya), and in other countries such as China (Lao chan), Malaysia (Beatris), Indonesia (Klappa, Kampit) and Mexico (San Antonio). Ore is associated with limy skarns which, in places, are superimposed on the early magnesian skarns. The deposits are related to biotite granites and to granitoids of the relatively high basicity. They are directly localized at the contact between the massifs and enclosing sedimentary strata which comprise limestone and dolomite beds, or at some distance away from the contacts, though within the contact zone of the intrusions.

Ore bodies have concordant sheet-like and lenticular as well as cross-cutting pipe-like, or, more rarely, wein-like shapes. The ores consist either of tin, or may be complex (Sn – W, Sn – Cu, Sn – Pb – Zn). Main ore minerals are magnetite, cassiterite, scheelite, pyrrhotite, arsenopyrite, pyrite,

chalcopyrite, sphalerite and galena; gangue minerals are represented by relics of limy skarn minerals (garnet, pyroxene), rarely, magnesian (forsterite), also by tremolite, fluorite, tourmaline, actinolite, phlogopite, muscovite; stannite, bismuthine and grey ores as well as feldspar, quartz and carbonates are subordinate.

The ore deposition involved several stages, namely: skarn-magnetite (600-360 °C), cassiterite-K-feldspar and quartz-sulfide (450-160 °C). Alteration of host rocks manifests itself in skarnitization, actinolitization and tremolitization. High-temperature associations which include magnetite, cassiterite, pyrrhotite and arsenopyrite are more distinct at deeper horizons of the deposits and near the intrusions; sulfides develop at the upper horizons and at flanks.

KITELYA DEPOSIT is located in Karelia. The area is composed of granite-gneisses, schists and marmorized limestones of the Precambrian Pitkyaranta formation. These form a cupola-like structure cut by the Samgin intrusive massif. The massif is
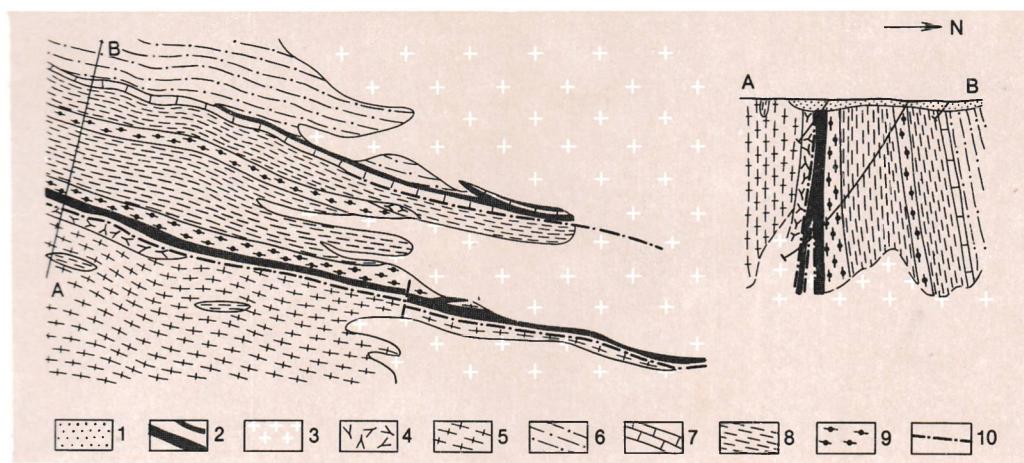
Fig. 69. Schematic geological map of the eastern part of the Kitel ore field. (After R. and V. Khazov):

1 – Quaternary sediments;
2 – ore skarns;
3 – granite of the second phase;
4 – arterite migmatites;
5 – plagiomicrocline gneiss-granites and shady migmatites;
6 – biotite-quartz schists and gneiss-schists interbedded with quartzites;

7 – marmorized and skarnized limestones with interlayers of skarns;
8 – amphibole schists and feldspathic amphibolites;
9 – interbedding of various schists, amphibolites and thin layers of skarnized limestones;
10 – faults

composed of rocks related to three phases of emplacement (from 1 650 to 1 420 m.y.) united into one complex of rapakivi granites and their vein differentiates. The deposit is localized at the contact of the second-phase granites, but its ore bodies being confined to the horizons of skarnized limestones are traceable across the intrusive contact (Fig. 69).

The main skarn-ore sheet-like body showing a steep dip is restricted to the lower horizon of carbonate rocks (10-15 m thick). This body consists of ore columns which are controlled by flexures of beds and by jointing. The ores are complex (Sn – Zn – Cu). Main ore minerals include magnetite, sphalerite, chalcopyrite and cassiterite; gangue minerals are represented by diopside, hedenbergite, andradite-grossular, vesuvian, actinolite, quartz, calcite and fluorite; pyrite, pyrrhotite, sulphosalts and scheelite as well as topaz, micas and chlorite are subordinate. Ore structures are banded, brecciated and disseminated.

The ore deposition involved four stages: (1) skarn-magnetite (580-440 °C), associated with rapakivi granites of the second phase; (2) cassiterite feldspar (420-380 °C), which

followed the intrusion of aplite-like granite dikes; (3) quartz-sulfide (350-300 °C); (4) post-ore chlorite-calcite (220-140 °C). The skarn body exhibits a zonal pattern in a cross-section: (1) skarnitized limestones (3-6 m); (2) barren amphibole-pyroxene skarns (up to 20 m); (3) pyroxene and amphibole skarns (up to 5-6 m) with magnetite-sulfide ore; (4) pyroxene-garnet skarns (2-3.5 m) with disseminated magnetite, cassiterite and sulfides; (5) calcite-pyroxene skarns with magnetite.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal deposits, which are most widespread among tin deposits are known in the Soviet Union in Chukot Peninsula (Valkymei), Yakutia (Deputatskii, Ege-Khaya), Primorski Krai (Khrustalnyi), Amur river region (Solnechnyi), Transbaikal region (Khapcheranga, Sherlovaya Mountain), and in other countries: Great Britain (Dollcoats, Crofty), Canada (Mount Pleasant), Australia (Mount Bishof). They are related to minor intrusions of

comparatively basic hybrid granitoids, less commonly, to plutons of normal granitoids. Lamprophyre, diorite and diabase porphyry dikes with which the above-mentioned tin deposits are associated in time and space, are typical for the area. The deposits are localized in granitoid massifs, more often in adjacent sandy shales strata. Ore bodies are mainly represented by veins in steep shear zones, by vein-like bodies in crush zones, by stockworks or, rarely, pipe-like bodies at the intersections of faults or fissures. The ore veins extend for hundreds of metres along the strike and for 300-350 m along the dip; their thickness varies from 0.1 to 2-3 m. They frequently form a vein field extending for several kilometres along the strike and up to 1 000 m along the dip.

The main ore minerals include cassiterite and pyrrhotite; gangue minerals are quartz, tourmaline, chlorite; arsenopyrite, chalcopyrite, sphalerite, galena and stannite as well as adular, sericite, manganosiderite, manganankerite and calcite are subordinate. Cassiterite occurs as long prismatic and needle-like crystals. Enclosing rocks are hydrothermally altered to form quartz-tourmaline and quartz-sericite-chlorite metasomatites.

The ore deposition involved the following main stages: (1) tourmaline-quartz or chlorite-quartz; (2) cassiterite-quartz (550-300 °C); (3) sulfide (350-200 °C); (4) galena-sphalerite-carbonate (320-200 °C); (5) carbonate-fluorite-quartz (250-30 °C). Vertical zonality manifests itself in the replacement (from bottom to top) of the tourmaline- and chlorite-cassiterite ores of a low sulfide content by sulfide ores. Horizontal zonality is manifested in the fact trat the central zone (commonly above the granitoids) consists of tourmaline-cassiterite ores, the middle part is composed of chlorite-cassiterite ores and the outer part, the most distant from intrusive body, consists of carbonate-sulfide ores with sulphosalts.

Two ore formations first studied by S. Smirnov, are recognized among plutonogenic hydrothermal deposits: (1) cassiterite-silicate-sulfide formation whose deposits are rather common (Valcumei in Chukot Peninsula, Deputatskii, Ege-Khaya in Yakutia, Khrustalnyi in Primorski Krai, Khapche-

ganga in Transbaikal region; Dollcoats, Crofty in Great Britain; Mount Pleasant in Canada); (2) cassiterite-sulfide formation, whose deposits are less commonly observed (Dalnii, Smirnovsk in Primorski Krai, Solnechnyi in Amur river region; Renison Bell in Australia; Menson Lodd in Malaysia).

Deposits of Cassiterite-silicate-sulfide Formation

DEPUTATSKII DEPOSIT is located in Yakutia. The area is composed of flat lying hornfelsed sandy shales of the Upper Jurassic age, forming the southern limb of the sublatitudinal striking syncline. The deposit is confined to a supra-intrusive zone of the Late Jurassic granitoid massif (143-138 m. y.). Numerous Upper Cretaceous (120-70 m. y.) dikes of quartz porphyry, diorite and diabase porphyries intrude two-mica and biotite-quartz hornfels.

There is a series of ore veins (in shear zones) having a length from tens to hundreds of metres and the thickness from 0.1 to 1.0 m. Stockwork zones of the same extension, whose width reaches tens of metres and mineralized crush zones being
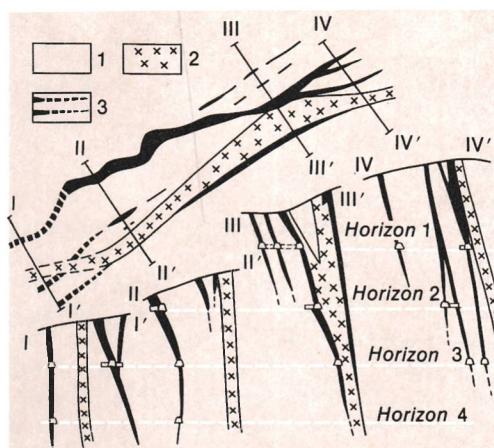
Fig. 70. Morphology of ore bodies and their control by lamprophyre dikes at the Deputatskii deposit. Sections and plan of Vein 34 on Level 2. (After B. Flerov):

1 – host rocks;
2 – lamprophyre dikes;
3 – ore bodies
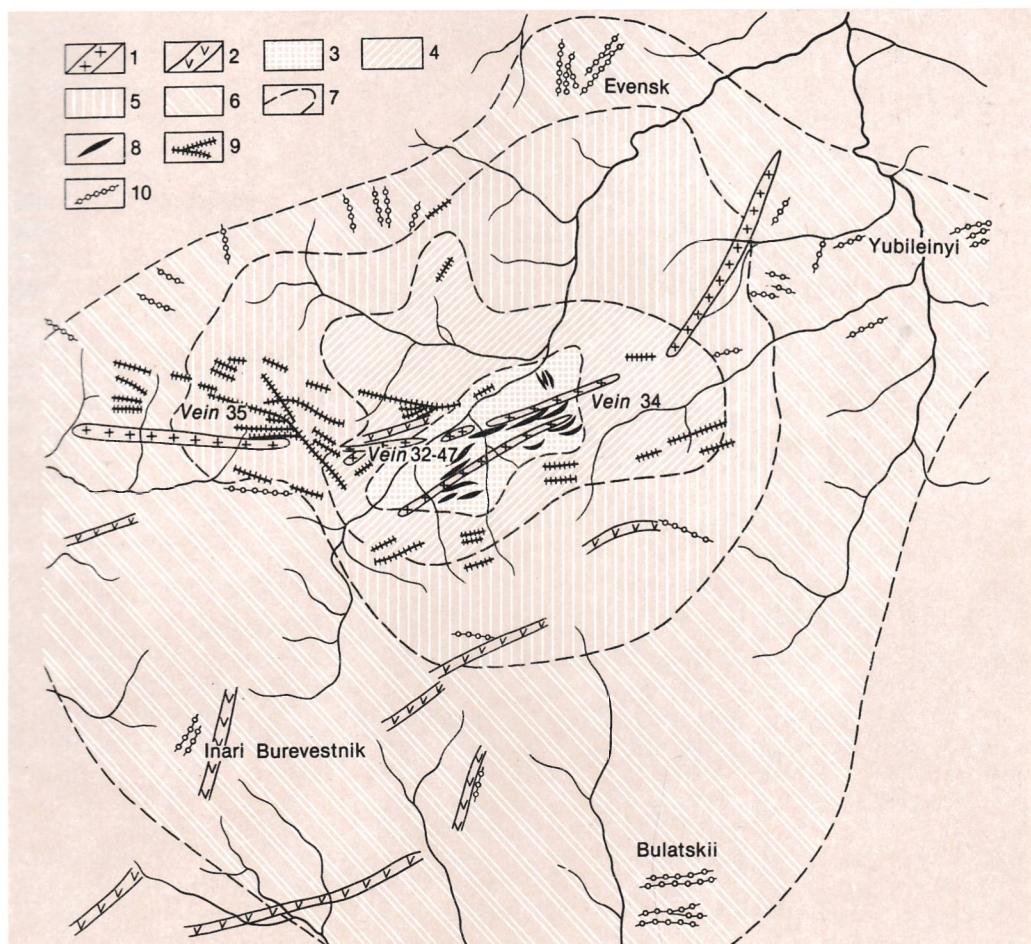
Fig. 71. Scheme showing a horizontal zonality of the Deputatskii deposit. (After I. Nekrasov):

1 – dikes of quartz porphyries;
2 – dikes of diorite porphyries and lamprophyres;
3-6 – zones of occurrence:
  3 – of tourmaline and cassiterite-quartz-tourmaline veins;
  4 – of essentially cassiterite-quartz-tourmaline and quartz-sulfide veins;
  5 – of quartz-sulfide veins with chlorite and carbonate;
6 – of quartz-carbonate veins with galena and sphalerite;
7 – contours of ore field and individual zones;
8 – tourmaline and quartz-tourmaline veins with cassiterite;
9 – quartz-chlorite and quartz-sulfide veins with cassiterite;
10 – quartz-carbonate veins with galena and sphalerite

traceable for many hundreds of metres, with thickness up to 10 m are also known. The ore bodies have mainly a sublatitudinal strike and a steep dip (Fig. 70). There is a sharp decrease in the amount of veins and in their thickness along the dip; the veins either pinch out or merge with depth. Stockworks occur in the upper horizons. Ore is distributed irregularly. Ore columns are established at places where the main ore veins change their strikes and where feathering fissures are observed.

Main ore minerals include cassiterite and pyrrhotite; gangue minerals are represented by quartz, tourmaline and chlorite; wolframite, arsenopyrite, pyrite, chalcopyrite, sphalerite, marcasite as well as manganosiderite, siderite, ankerite, sericite, axinite and topaz are subordinate. Ore is characterized by brecciated, banded, drusy and cocarde structures.

The ore deposition of the hydrothermal phase (which developed after a weak tin-bearing greisen phase) involved several

stages: (1) quartz-tourmaline; (2) cassiterite-silicate-quartz; (3) sulfide (pyrrhotite); (4) sulfide-carbonate; (5) carbonate. Host rock alterations consisted chiefly of silicification, tourmalinization and cloritization. According to I. Nekrasov and B. Flerov, a primary zonality can be manifested in relation to the unexposed cupola-like erosion uplift of granitoids: the central zone consists of cassiterite-quartz-tourmaline ores whose lower limit starts at a distance of 100 m from the contact of the granites, the middle zone is composed of cassiterite-chlorite-sulfide ores whose boundary lies at a distance of 700-800 m from the same contact, and the peripheral zone consisting of carbonate-sulfide ores, which are far more distant from the intrusive body (Fig. 71).

Deposits of
Cassiterite-sulfide Formation

The ores in deposits of this formation include almost all minerals typical of the cassiterite-silicate-sulfide formation, but their quantitative role is different. Thus, iron silicates (tourmaline, chlorite) are present in them in quantities not exceeding 1%.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

Volcanogenic hydrothermal deposits are known in the Soviet Union in Maly Khingan (Jalinda, Khingan), and in other countries in Bolivia (Llallagua, Potosi, Oruro), Mexico (Duranga, Elm Santin) and Japan (Axenobe). The deposits are related to K-rich acid rhyolites and to moderately acid members of andesite-rhyolite formation (dacite, quartz latite) which belong to Alpine and partly to Kimmerian epochs. They occur predominantly in volcanic rocks and are associated with subvolcanic, vent and, less commonly, effusive facies. The deposits are confined to volcanic domes, vent and extrusive structures as well as to synvolcanic faults and fissures.

Ore bodies are represented by branching veins, less commonly, by mineralized crush zones and stockworks. The ore veins vary in thickness from 0.1 to 2-3 m, being about 1 m on the average. They are traceable for many hundreds of metres along the strike and dip. But usually even on the major deposits, where ore bodies extend for 700-800 m to depth, the productive interval does not exceed 250-300 m. The veins comprise rich ore columns. The ores are tin-bearing, often complex (Sn–Ag, Sn–Pb–Zn). Mineral composition is also complex. The main ore minerals include cassiterite (locally wood tin), stannite, bismuthinite, arsenopyrite, pyrrhotite; gangue minerals are represented by quartz, tourmaline, sericite; frankeite, wolframite, chalcopyrite, sphalerite, galena, pyrargyrite, argentite, boulangerite, jemsonite, grey ore, native silver, hematite as well as tridymite, kaolinite, dickite, alunite, opal, fluorite, barite and chalcedony are subordinate. Hydrothermal alteration of enclosing volcanic rocks consists of tourmalinization, propylitization, silicification, sericitization and argillization.

The ore deposition occurred mainly under subvolcanic environments at a depth from 100-200 to 700-800 m from the surface. It involved several stages: (1) quartz-tourmaline-cassiterite; (2) stannite; (3) sulfide; (4) galena-silver; (5) alunite-chalcedony. Typical is an abrupt drop of the temperature of ore emplacement: from very high temperatures at the early stages to low temperatures at the late one. It results in superposition of mineral associations produced at various temperatures (telescoping).

Vertical zonality is expressed in development of cassiterite and bismuthinite, locally with wolframite, at lower horizons, while at upper horizons dominate stannite, silver minerals and abundant barite. Ore veins with cassiterite and silver minerals are typical of the central parts of the deposits, their peripheries, on the other hand, contain veins with galena and silver minerals. Three ore formations are recognized among tin volcanogenic hydrothermal deposits: (1) cassiterite-silicate-sulfide; (2) cassiterite-sulfide; (3) wood tin.

Deposits of Cassiterite-silicate-sulfide Formation

LLALLAGUA DEPOSIT is located in Bolivia. The annual production makes up 4 000 tons of tin, its average content being 0.5%. The

area is composed of Paleozoic and Cretaceous sediments forming an anticline complicated by faults of different strikes. The sedimentary rocks are cut by an ethmolith-like subvolcanic body of the Neogene age (9.4 m. y.). The body consists of quartz latites and their breccias which belong to the andesite-liparite formation. Subvolcanic and enclosing rocks are cut by several systems of fissures.

Ore bodies occur as steeply dipping veins, commonly branching, trending mainly north-eastward and north-westward, locally dipping towards each other (Fig. 72). Mineralization in the veins is irregular. Ore columns – the richest parts of the deposit (Sn is up to 25%), vary in extension from 400 to 700 m along the strike and from 250 to 600 m along the dip.

Main ore minerals include cassiterite, bismuthinite, pyrrhotite and pyrite; quartz, tourmaline and siderite are gangue minerals; frankeite, stannite, arsenopyrite, wolframite, sphalerite, chalcopyrite and sericite are subordinate. Ore structures are massive, reticulate, brecciated, banded, drusy and disseminated; textures are crystalline and colloform.

The ore deposition involved five stages: (1) quartz-bismuthinite-cassiterite; (2) pyrrhotite (with frankeite); (3) pyrrhotite-arsenopyrite (with stannite); (4) pyrite-marcasite; (5) sphalerite. Host rocks, particularly latite porphyries, are tourmalinized, sericitized, and silicified. According to F. Alfeld and F. Turner, horizontal zonality represented by a concentric pattern is manifested in the fact that the central zone (at a depth of 250-450 m from the surface), composed of cassiterite produced at the high-temperature early stage, is surrounded at the lower and upper horizons and at the flanks of the deposit by a sulphosalt-rich (including stannite) sulfide zone. Llallagua ores were formed at a depth of about 800 m.

Deposits of Cassiterite-sulfide Formation

THE POTOSÍ tin-silver ore deposit in Bolivia is the most representative among deposits of this formation. The deposit is described in the chapter "Silver Deposits".
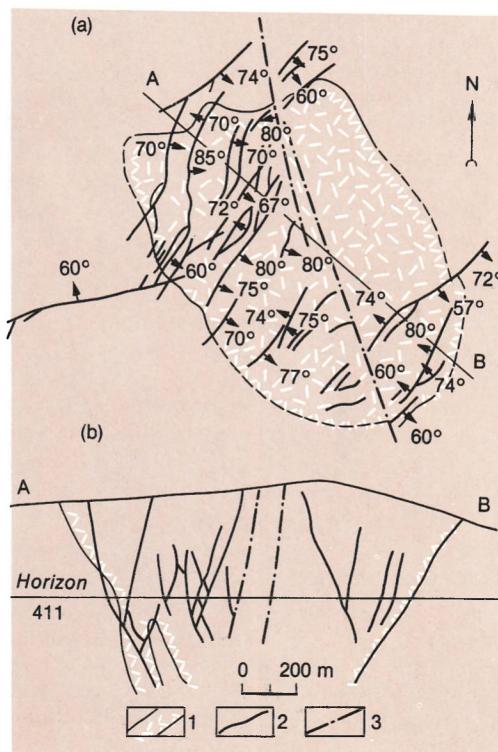
Fig. 72. Plan (*a*) and section (*b*) of the Llallagua vein system, Bolivia, (After F. Turner):

1 – quartz porphyries;
2 – ore veins;
3 – faults

Deposits of Wood-tin Formation

Tin ore deposits containing wood tin (colloform cassiterite) are small but in some cases they form a source for placers. Since these near-surface deposits are closely related to acid effusive rocks (K-rich rhyolite), this ore formation is also called a rhyolite one (Jalinda in Maly Khingan, El Santo in Mexico). The ore deposition occurs rapidly, in one or two stages. The ore zonality is not typical of these deposits.

PLACER DEPOSITS

Tin-bearing placers are known in the USSR in Chukotka (Pyrkykai), Yakutia (Deputatskii), Primorski Krai (Voskresenskii), and abroad in Malaysia (Kinta, Perak), Indonesia (Bangka), Thailand (Chanwat), China (Nyu Shi po), Vietnam (Tin-Tuk),

Brasil (Rodondi), Zair (Manono-Kitotolo) and Nigeria (Bauchi). These placers were formed as a result of disintegration of primarily pegmatite, greisen and partly hydrothermal tin deposits.

Stockwork ore deposits appear to be favourable for formation of placers. Eluvial, diluvial, alluvial and seabeach cassiterite placers are distinguished.

Eluvial Placers

These are most widely distributed in the countries with hot and humid climate. They are formed as a result of chemical weathering that penetrates to a depth of 200 m. Such placers differ from the weathering crusts in the enrichment of a loose material with cassiterite which occurs as angular grains. Apart from cassiterite, the eluvial placers may contain columbite, tantalite, wolframite, scheelite, gold, topaz, tourmaline, zircon and magnetite. The thickness of such placers makes up to 20-30 m, occasionally up to 60-80 m. The average content of cassiterite is 0.5-1.5 kg/m^3, though in the rich lower levels it reaches 5-6 kg/m^3.

The eluvial placers often serve as the formation source of the other types of placers representing, so to say, an intermediate cassiterite collector. Eluvial placers are quite important in the world production of tin concentrates.

Diluvial Placers

These represent a continuation of eluvial placers when the latter are displaced downslope and in the case of a more complete sorting of the material. The distribution of cassiterite is extremely irregular, its relatively high concentration is observed in the lower parts of the section. The thickness of the placers reaches first tens of metres. Mineral composition of the diluvial placers is the same as that of eluvial ones and it is determined by the composition of bedrock sources.

Alluvial Placers

These placers are most common and occur in different climatic zones.

Owing to the friability of cassiterite, the alluvial placers are rarely traceable for more than 5-10 km from bedrock sources. They are characterized by a relatively uniform distribution of cassiterite, well sorted material and by a tendency of cassiterite to concentrate at the base of the sedimentary stratum (close to bed rock). Therefore, the structure and composition of bed rocks affect cassiterite accumulation. Favourable in this respect are karstified limestones, trough-like depressions and valley floor bends.

Where the main valley is linked with tributary placers, there appear complex clusters showing a high content of cassiterite (up to 15-20 kg/m^3) and a larger thickness of the bed. The thickness of tin-bearing beds as well as of overlying barren sediments varies from fractions of a metre to first tens of metres, 0.5-1 m as an average. The cassiterite content varies from 0.2-0.3 up to several kilograms per cubic metre, 0.6-0.8 kg/m^3 as an average. Apart from cassiterite, a heavy fraction may contain rutile, wolframite, gold, tantalite, columbite, magnetite, pyrite, hematite, garnet, topaz, zircon, fluorite and anatase. Alluvial placers include the valley placers of the highest commercial value and terrace placers. These may be both ancient (buried), which play a leading role, and recent.

DEPUTATSKII DEPOSIT. The cassiterite placers of the Deputatskii River and its tributaries are closely associated with bedrock sources through the tin-bearing diluvium and eluvium (Fig. 73). The river valleys, asymmetric in a cross section are well developed; several terraces are distinguished. Placers of the valley type are predominant. They fill in the flood plain completely. The flood plain section is as follows (from bottom to top): (1) bed rocks (sandstone, schists), with weakly undulated surface (bed rock); (2) pebble beds, being moderately rounded (payable bed, 4-5 m thick); (3) alluvial silt (2-3 m) with ice lenses; (4) vegetation layer (0.2 m). Cassiterite distribution as is seen in the placer plan, is rather uniform; the highest cassiterite accumulation is at the lower part of the payable bed and in the fissured upper part of the bed rock. Predominant is a large fraction (from + 3.6 mm up to − 16 mm) consisting of cassiterite + tourmaline intergrowths,
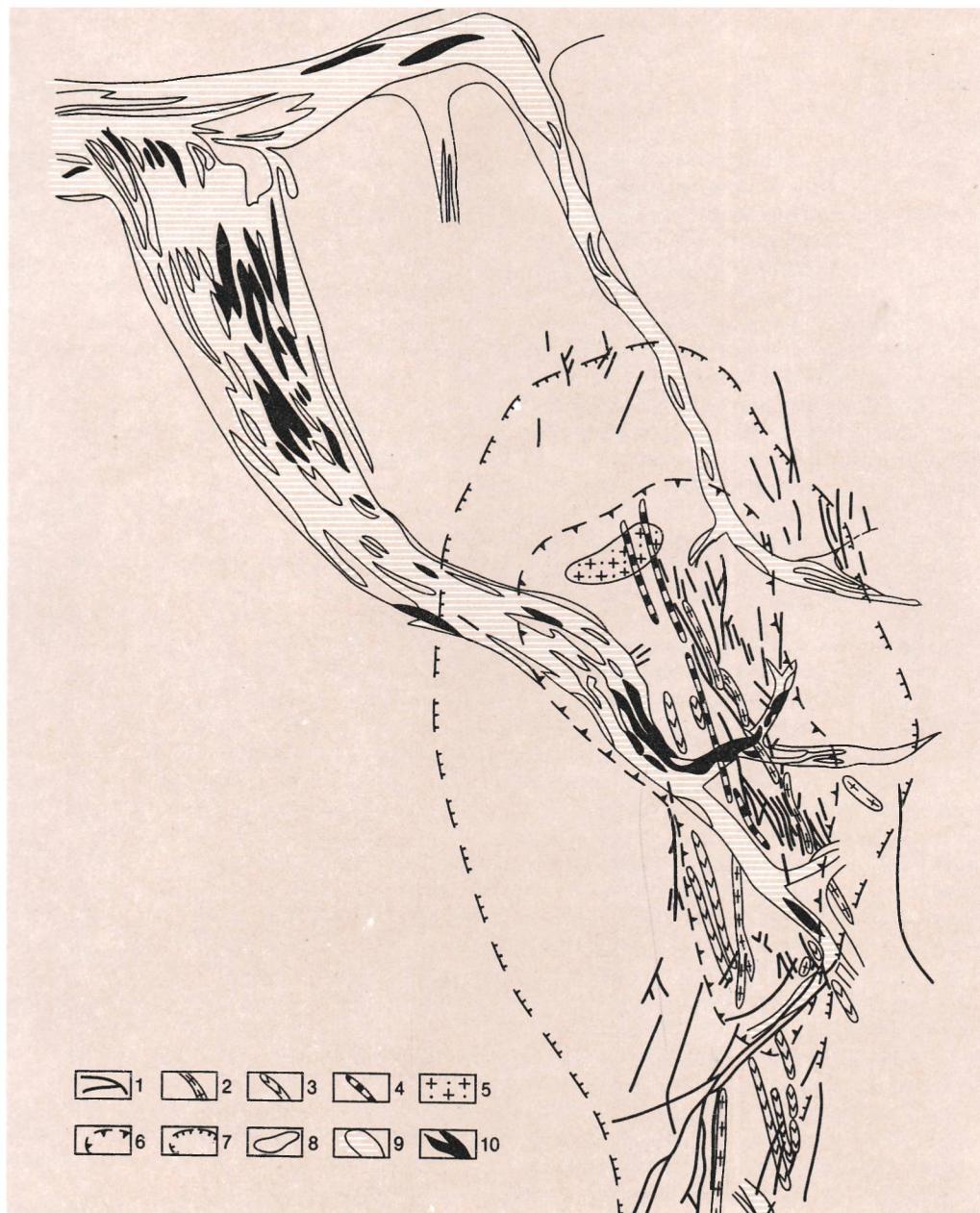
Fig. 73. Scheme showing location of ore bodies and tin-bearing placers of the Deputatskii deposit:

1 – ore bodies;
2-4 – dikes:
  2 – of quartz porphyry and felsite;
  3 – of porphyrite;
  4 – of lamprophyre;
5 – greisenized sandstones and shales;
6-7 – zones of contact metamorphism:

6 – of intensive metamorphism;
7 – metamorphism of medium intensity;
8-10 – sites of tin placers:
  8 – with unpayable cassiterite contents;
  9 – with payable ordinary contents;
  10 – high-grade placers

quartz grains, chlorite flakes, occasionally hornfel fragments with quartz-cassiterite veinlets.

Seabeach Placers

Three types are distinguished among these placers: (1) old seabeach placers of high terraces; (2) recent seabeach placers; (3) placers of old and recent river valleys and flat interfluves buried on the sea bottom. The first two types are insignificant, while the third type is becoming more and more important. In fact, these are flooded alluvial, diluvial and eluvial placers originated as a result of gradual subsidence of land. They are traceable for up to 5-15 km away from the present-day shore line, which corresponds to a depth of 30 m from the sea level. These placers are mined in the countries of the South-East Asia.

13 TUNGSTEN DEPOSITS

Tungsten was discovered by the Swedish chemist C. Scheele in 1781, and at the end of 19th century it began to be used for steel alloying. Tungsten increases hardness, refractoriness, elasticity and acid resistance of steel. Apart from alloying, tungsten is used in the production of superalloys and hard alloys (pobedite, carbide and boride); it is also utilized for production of electric bulbs. Tungsten is obtained from tungsten, molybdenum-tungsten, tin-tungsten, bismuth-tungsten, and polymetallic-tungsten ores.

The cost of one ton of WO_3 in a concentrate reaches 10 000 US dollars. In the capitalist and developing countries the production of tungsten concentrates in 1975 made up 26 thous. tons; measured reserves – 630 thous. tons WO_3, total reserves – 1160 thous. tons WO_3. Unique bedrock deposits (Sangh-Dong in South Korea; Panasqueira in Portugal) comprise more than 250 thous. tons of WO_3, large deposits – 250-100 thous. tons, medium ones – 100-15 thous. tons, small ones – less than 15 thous. tons. Rich ores contain over 1% WO_3, average ores – 1-0.3%, poor – 0.3-0.1% and low-grade ores – less than 0.1%. The placers are considered to be of commercial value if WO_3 content is no less than 300-200 g/m^3.

GEOCHEMISTRY AND MINERALOGY

Five stable tungsten isotopes with mass numbers 180, 182-184 and 186 are known. This metal occurs in 4- and 6-valent compounds, of which the variety of the highest valency is most stable in natural conditions. The crustal abundance (clarke) of tungsten is $1.3 \cdot 10\%$, its concentration coefficient being 5 000. The crustal abundance of various magmatic rocks varies insignificantly, it slightly decreases in ultra-basic rocks $(1 \cdot 10^{-5}\%)$ and increases in acid $(1.5 \cdot 10^{-4}\%)$ rocks. Crustal granitic magma, oversaturated with alumina with high acidity and a relatively high content of volatiles (fluorine, boron) is the source of the commercial endogenous tungsten concentration. Tungsten is evacuated from magmatic chambers by gas-hydrothermal moderately acid fluids. It is partly transported as oxyhaloids but mainly as heteropolycompounds of tungsten, alkaline metals, and silica, for example of $SiO_2 \cdot 12WO_3 \cdot 8KOH \cdot 10H_2O$ type. Precipitation of tungsten minerals starts at the temperature not higher than 350-400 °C.

In exogenous conditions tungsten minerals are sufficiently stable and may give rise to placers. During sedimentation some tungsten accumulation occurs in the marine terrigenous, less frequently carbonate deposits, enriched with Fe, Mn and coaly matter. This is confirmed by tungsten content of up to several per cent in the infiltration and exhalation iron-manganese formations. In the continental environment a relatively high tungsten content is occasionally observed in coals and in water of salt lakes. In metamorphic processes tungsten may be segregated as scheelite owing to regeneration of the initially sedimentary dispersed mineralization.

Among tungsten minerals, wolframite $(Mn, Fe)WO_4$ (60.5%), ferberite $FeWO_4$ (60.5%), hübnerite $MnWO_4$ (60.7%) and scheelite $CaWO_4$ (63.9%) are of commercial value. Wolframite and hübnerite make up a total of 75% of the world production, and scheelite constitutes about 25%. In the oxidation zone there occur tungstite

H_2WO_4 (74%), hydrotungstite $H_2WO \cdot H_2O$ ~9~) and tungomelane – tungsten-containing psilomelane (W up to 4-7%).

METALLOGENY

Endogenous tungsten deposits owe their origin to postmagmatic granitic magma. They formed primarily in the late phase of the geosynclinal stage, as well as a result of tectono-magmatic activization of the platforms. Magmatism producing the tungsten ore is associated with tectonic zones (orogenic, median masses), which are characterized by a continental type of the crust. Continental placers of tungsten minerals were deposited at platform stage.

In the history of geologic development of the Earth's crust, as is in the case of molybdenum and tin, the number of tungsten deposits increased with time from old metallogenic epochs to younger ones. In the Archean and Proterozoic times small pegmatitic (Silver Hill in the USA) and skarn deposits (Brezhu in Brasil, Igohellen in Sweden) originated. Larger hydrothermal deposits were formed during Caledonian (Boguty in Kazakhstan). During the Hercynian epoch there appeared large skarn, greisen and hydrothermal deposits in various provinces (Akchatau in Kazakhstan, Ingichke in Central Asia, Panasqueira in Portugal, King Island in Australia). But the Kimmerian and Alpine epochs came to be most productive for various endogenous as well as exogenous (placer) tungsten deposits (Iultin in Chukotka, Bom-Gorkhon in the Transbaikal region, Tyrnyauz in the Caucasus, Sangh-Dong in South Korea).

TYPES OF COMMERCIAL DEPOSITS

The following types of tungsten commercial deposits are distinguished: (1) skarn; (2) greisen; (3) plutonogenic hydrothermal; (4) volcanogenic hydrothermal; (5) placer.

No commercial value has been established for the metamorphogenic deposits of stratiform ores of the scheelite composition in the Precambrian crystalline rocks in Austria (Tuks, Felbertal), Portugal (Lagoasa), or Norway (Bindal).

GREISEN DEPOSITS

Greisen tungsten deposits frequently containing molybdenum or tin are known in the USSR mainly from the Transbaikal region (Spokoininskii) and Kazakhstan (Akchatau, Kara-Oba); abroad from the GDR (Şadisdorf, Pechtelgrün); Czechoslovakia (Činovec, Krupka); France (Montebrasse); Mongolia (Yugodzyr, Bayanmod); China (Pyaotan, Sinkiangshang) and from Australia (Wolfram-Camp, Terrangton). These are confined to the apical dome-like zones of leucocratic, occasionally pegmatoid granites extending for 300-500 m (endogreisens) as well as in the hornfelsed rocks of the top for 1 200-1 500 m (exogreisens). The shape of the greisen deposits is that of a stock which originated during mass metasomatism, and of stockworks, less frequently veins using prototectonic joints. Greisen-vein bodies extend along the strike from some tens of metres to 1 000 m and more, and along the dip for 300-400 m, the thickness being 0.3-0.5 m, less frequently up to 1 m. Between them there are veinlet-disseminated greisen zones having swells and pinches of a variable thickness.

Tungsten ores are mainly associated with quartz-topaz, quartz-mica and quartz greisens. The main ore minerals are wolframite, frequently molybdenite, cassiterite; the subordinate ones include magnetite, bismuthinite, pyrrhotite, pyrite, chalcopyrite, sphalerite and galena; the main gangue minerals are represented by quartz, muscovite, biotite, acid plagioclase and microcline whereas non-metallic subordinate – by tourmaline, topaz and fluorite. The host rocks are usually greisenized as well as muscovitized, biotitized and silicified.

Ore deposition occurred in several stages, from which the first two are of the greisen type accompanied by wolframite, molybdenite, cassiterite and bismuthinite segregation, the third one – quartz-wolframite, the fourth one – sulfide stage, the fifth one is the post-ore quartz-carbonate stage. The temperature interval of the ore emplacement is from 540 to 300 °C, as in the case of molybdenum greisen deposits. A vertical zonality manifests itself in a decrease of the amount of topaz
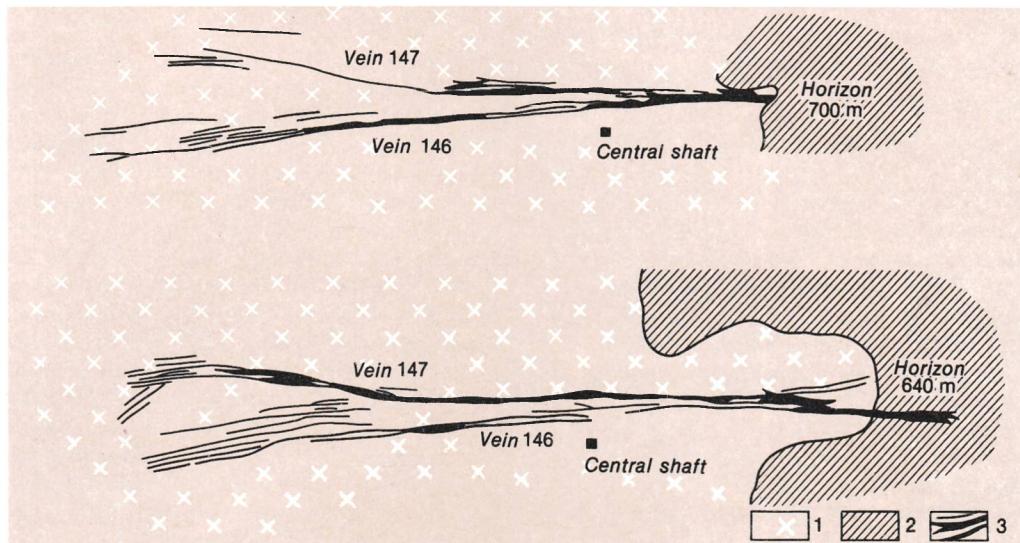
Fig. 74. Structure of vein swarm of the Akchatau greisen deposit. (After A. Shcheglov and T. Butkevich):

1 – adamellites;   *2 – sandstones;*   *3 – greisen and quartz veins*

with depth, an increase of mica and quartz quantity as well as in the lower tungsten and molybdenum content at deeper levels and sometimes in the increase of the tin content. The tungsten greisen deposits were emplaced in the orogenic geosynclinal zones and in the areas of the activization of ancient folding and platforms at a depth of 5 to one km from the earth surface, the vertical span of the mineralization being about 300-500 m.

AKCHATAU DEPOSIT is located in Kazakhstan. The deposit area is composed of the Silurian, Devonian and Lower Carboniferous volcanic and sedimentary rocks hornfelsed in the exocontact zone of the Late Permian Akchatau granitic massif. The massif is of a complex structure and was formed in three phases: (1) coarse-grained granite composing the dome to which the deposit is confined; (2) medium-grained granites; (3) fine-grained granites. Aplite dikes are also observed. There are over 300 greisen-vein ore bodies of several types confined to the shear joints (Fig. 74). Thick (0.1 up to 40 m) greisen bodies of a zonal structure are of the most commercial value. These strike almost from north to south and

dip steeply (70-80°). The bodies exhibit a complex dendritic structure.

Predominant are quartz and quartz-topaz greisens containing the bulk of tungsten and molybdenum reserves. The main minerals are wolframite, molybdenite and pyrite; the non-metallic minerals include quartz, muscovite and topaz; the subordinate minerals are represented by scheelite, bismuthinite, sphalerite, chalcopyrite and cassiterite as well as by fluorite, tourmaline, biotite and feldspars. Wolframite is distributed irregularly – mainly in the axial and selvage portions of the greisen veins. The ore is characterized by banded, drusy and disseminated structure and by hypidiomorphic, allotriomorphic and corrosion textures as well as by the texture of mutual boundaries. Ore emplacement occurred during the main, greisen stage, accompanied by metasomatic alteration of the enclosing granite and giving rise to near-vein zones of quartzose, quartz-topaz, quartz-micaceous greisens and greisenized granites. Quartz-sulfide veins and veinlets were formed at the hydrothermal stage. The endogenous zonality is expressed by a change of quartz-topaz greisens at depth and on the

flanks to quartz-micaceous and quartz greisens. Tungsten and molybdenum content also decreases with depth.

SKARN DEPOSITS

In the USSR these deposits are known from Primorski Krai (Vostok-II), Central Asia (Ingichke, Chorukh-Dayron, Koitash) and from the Caucasus (Turnyauz); abroad from South Korea (Sangh-Dong), China (Khuanpodi, Ilu), Canada (Emerald-Feney), the USA (Pine Creek) and from Australia (King Island). These are confined to the garnet-pyroxene and other calcareous skarns which are formed at the contact of granitoids with carbonate rocks, at some distance from this contact and, less frequently, in granitoids. The ores occur as sheet-like, lenticular, pocket-, pipe- and vein-like bodies. Their size makes up hundreds of metres – first kilometres along the strike, some tens of metres up to 800 m and more along the dip, the thickness being 1-2 to 50 m. The main ore minerals are scheelite, occasionally molybdenite; the subordinate ones include cassiterite, bismuthinite, magnetite, pyrrhotite, pyrite, arsenopyrite, wolframite, chalcopyrite, sphalerite and galena. The main non-metallic minerals are garnet, pyroxene, plagioclase, quartz; the subordinate – epidote, chlorite and carbonates.

Ore deposition in the tungsten skarn deposits is a continuous process involving 5-6 stages, among which the main stages are as follows: skarn pyroxene-garnet (600-210 °C) stage in which early scheelite is segregated (450-300 °C); quartz-sulfide (450-110 °C) one with late scheelite (160-110 °C) and barren quartz stage (130-80 °C).

The skarn tungsten deposits are associated with moderately acid intrusions of the late geosynclinal stage and activization of folded zones and platforms. The depth of their formation is from 4 to one km. Among these deposits two main formations are distinguished: scheelite (Koitash, Vostok-II, Sangh-Dong) and scheelite-molybdenite (Tyrnyauz) ones.

Deposits of Scheelite Formation

VOSTOK-II DEPOSIT is in Primorski Krai. The deposit area is composed of the Upper Permian and Upper Triassic sediments cut by stocks of granites, granodiorites and granite-porphyry, as well as by diorite-porphyry dikes. The deposit is located at the north-western limb of the NE-striking syncline. The mineralization is confined to the contact zone between the granitoid stock and a bed of sandstones, hornfels and limestones. The ore body is represented by a sheet deposit of scheelite ores accompanied by apophyses. It occurs among skarns extending for 600 m north-eastwards and dipping steeply (50-88°) to north-west (Fig. 75).

Two types of ores are identified: scheelite-quartzose and scheelite-sulfide (scheelite-pyrrhotite and scheelite-pyrrhotite-skarn). In sheelite-quartz ores the main mineral is scheelite, the subordinate minerals include pyrrhotite, chalcopyrite, native bismuth and bismuthinite; the vein minerals are represented by quartz; muscovite and apatite are subordinate. In scheelite-sulfide ores the main minerals consist of pyrrhotite (70-80%), scheelite, arsenopyrite, chalcopyrite, bismuthinite and sphalerite; the subordinate minerals are native bismuth, gold and silver, as well as wolframite, stannite and cassiterite. The nonmetallic minerals are represented by pyroxene, actinolite, quartz and apatite. The ores are characterized by massive, brecciated, stringer and banded structures and by hypidiomorphic, allotriomorphic, corrosion textures and by a texture of mutual boundaries.

The ore deposition occurred in two stages: barren skarn stage associated with granodiorites (age 127 m.y.) and the ore stage (84 m.y.). These two stages are separated by the intrusion of diorite-porphyry dikes. Four substages are distinguished in the ore stage: (1) greisen one (with scheelite); (2) quartz-scheelite one; (3) sulfide stage; (4) quartz-calcite stage.

SANGH-DONG DEPOSIT is located in South Korea. The deposit area is composed of the Cambrian sequence of quartzite intercalated with limestone, sandstone and phyllite. They rest unconformably on the Precambrian
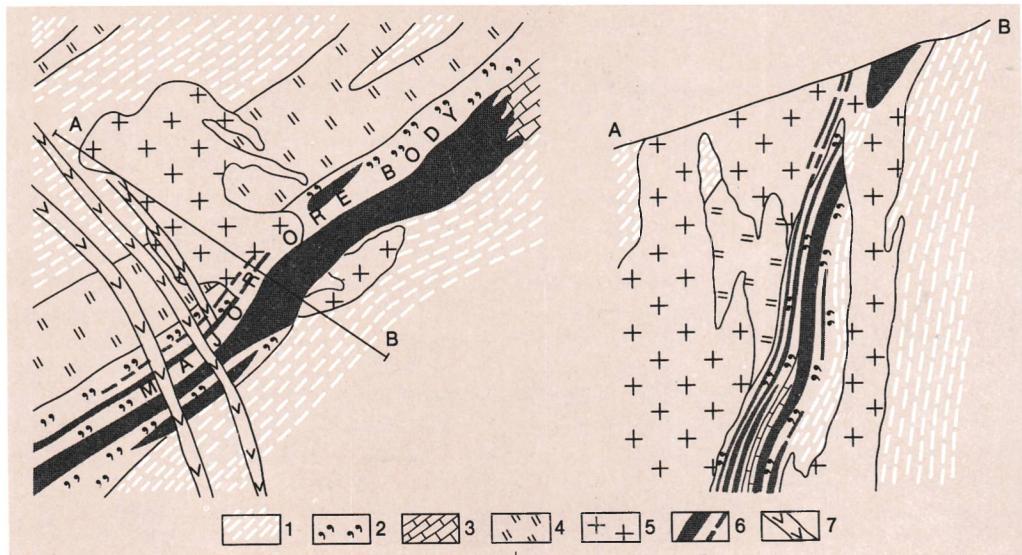
Fig. 75. Schematic geological map of the skarn deposit "Vostok-II". (After A. Ivakin and N. Lavrik):

1–sandstones;
2–biotite hornfels;
3–limestones;
4–chert and quartzites;

5–granites and granodiorites;
6–ore bodies;
7–porphyrite dikes
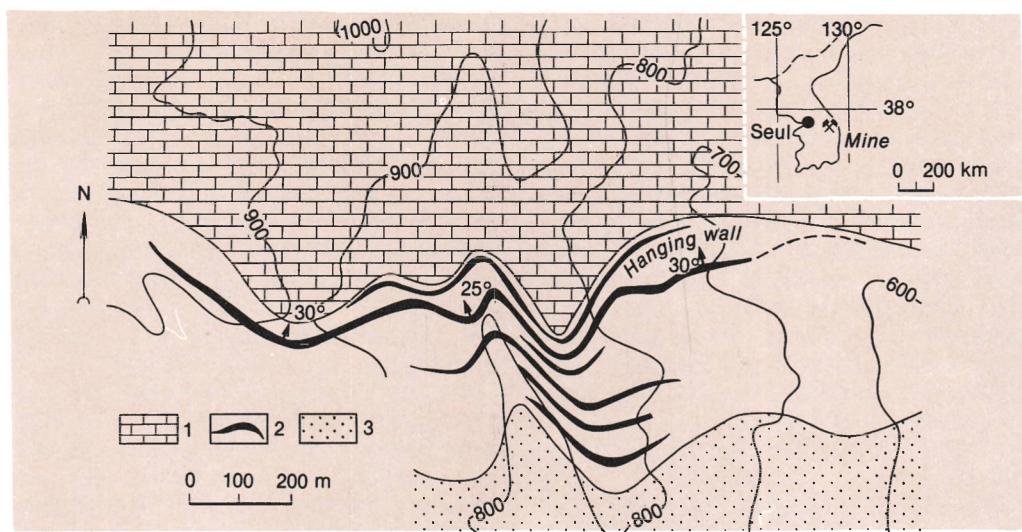
Fig. 76. Sketch map of the Sangh-Dong skarn deposit. (After I. Magak'yan):

1–limestones;   *2*–hornfels with skarn beds;   *3*–quartzites

metamorphic rocks and are overlain by Ordovician limestones. The Upper Cretaceous granite-porphyry stock crops out in the vicinity of the deposit. The Lower Paleozoic beds are crumpled into a sublatitudinal asymmetric syncline, to the gently dipping (15-30°) southern limb of which the deposit is confined. The folded structure is complicated by transverse downthrow faults developed mainly in the footwall of the deposit and serving as ore-feeding channels, subsequently rejuvenated.

The ore skarns form concordant sheet bodies among calcareous Cambrian rocks (Fig. 76). The main ore body confined to the inter-formational crush zone is traced along the strike for 1 000 m (of which 700 m are most intensely mineralized) and for 300 m along the dip, the thickness being 3-4.5 m.

The main ore minerals include scheelite, molybdenite, bismuthinite and pyrrhotite; the main gangue minerals are hornblende, biotite, diopside, quartz, sericite and chlorite; the subordinate minerals are represented by wolframite, pyrite, chalcopyrite, tetrahedrite, sphalerite, arsenopyrite and magnetite as well as andradite, epidote, fluorite, calcite and apatite. The ore is characterized by banded, veinlet-type and disseminated structures. The ore skarns formation involved 3 stages; skarn, molybdenite-scheelite and quartz-wolframite (independent veins) ones.

The ore zonality across the thickness of the ore bodies manifests itself in successive replacement of the metasomatic zones from the periphery towards the centre of the ore bodies: garnet-pyroxene skarns (WO_3 0.2-0.3%) are replaced by quartz-hornblende (1-2%) and then by quartz-biotite-chlorite-sericite (2%) metasomatites. In the central parts of the ore bodies, due to the abundance of quartz-ore veins, ore shoots are formed. A vertical zonality is expressed in a substitution (upward) of quartz-scheelite-hornblende paragenesis for quartz-scheelite-chlorite-sericite one; with depth molybdenum content increases whereas that of bismuth drops down.

*Deposits of
Scheelite-molybdenite Formation*

These deposits are described in the chapter "Molybdenum Deposits".

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal tungsten deposits, frequently with molybdenum and tin, are known in the USSR in Chukotka (Iultin), Transbaikal region (Bukuka, Antonovogorskii, Kholtoson, Bom-Gorkhon, Chikoi), Kazakhstan (Upper Kairakty, Boguty) and abroad in Portugal (Panas-queira), Great Britain (Cornwall), France (Belfort), Mongolia (Tumen-Tsokto), China (Lyandushang, Shanpin), Canada (Red-Rose) and Australia (Haberton). They are associated with domes of granitic massifs and granite-porphyry stocks being distributed mainly at the exocontact zone composed of hornfels and, less frequently, within the endocontact zone.

The ore occurs as veins, stockworks or stockwork zones. A series of veins (tens-hundreds) are confined to the system of persistent steeply dipping shear joints or tear faults often of contraction origin. The stockworks are related to minor jointing or cleavage. Individual ore veins extend for tens-many hundreds of metres, while their sworms are traceable for many kilometres along the strike and up to 300-500 m, occasionally 800 m and more along the dip. The thickness of separate veins varies from 0.1 to 4-5 m (in swells), the average thickness being 0.5-1 m. The stockworks are 400-500 to 1 000 m across; the stockwork zones being tens-first hundreds of metres wide are extending for several kilometres along the strike.

The main ore minerals are wolframite or hübnerite, occasionally scheelite; cassiterite, molybdenite, bismuthinite, arsenopyrite, pyrrhotite, pyrite, chalcopyrite, sphalerite and galena are subordinate. The main gangue mineral is quartz, the subordinate gangue minerals consist of tourmaline, muscovite, sodium plagioclase, microcline, topaz, fluorite, apatite, sericite, carbonates. The host rocks are greisenized, tourmalinized, berezitized, silicified and sericitized.

The main stages of mineral formation are as follows: (1) quartz-wolframite; (2) sulfide; (3) quartz-fluorite; (4) post-ore carbonate. Wolframite (or hübnerite) is segregated twice – at the first stage – as coarse columnar (up to 20 cm) crystals and at the third stage as fine tabular or acicular crystals. Formation of the entire mineral assemblage occurred at a 380-100 °C temperature interval, the ore was deposited at an interval of 380-200 °C. A horizontal zonality, frequently concentric, particularly in stockworks, manifests itself in appearance of high-temperature associations with wolframite in the central zone, of medium-
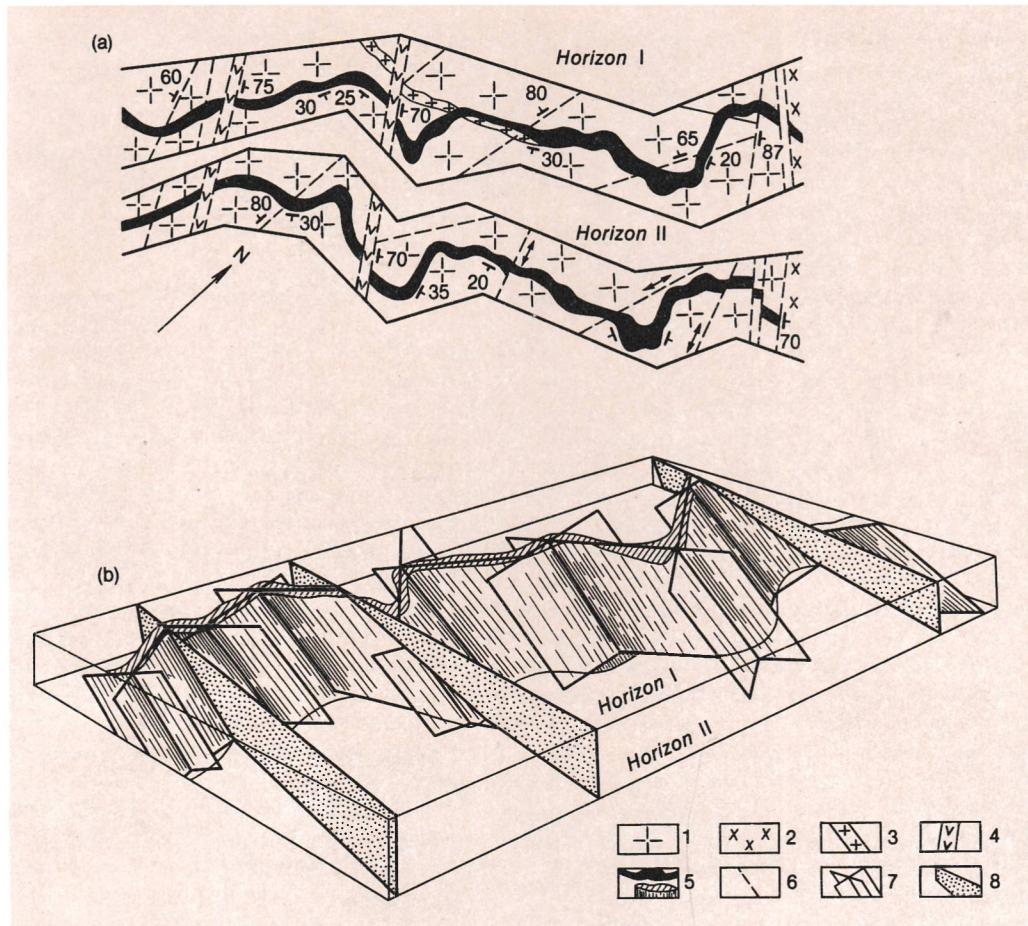
Fig. 77. Major ore vein of the Bom-Gorkhon deposit. (After E. Polyanskii and V. Starostin). Area of the combined horizon-to-horizon plan (a) and block diagram showing interrelations of main structural units of the deposit (b):

1 – porphyroid granites;
2 – granosyenites;
3 – aplites;
4 – diorite porphyrites;

5 – ore bodies;
6 – faults;
7 – planes of ore-enclosing fissures;
8 – post-ore fault planes

temperature sulfide ones in the intermediate zone, and of low-temperature quartz-fluorite associations in the peripheral zone. A vertical zonality may be both direct, expressed by the same substitution of the high-temperature mineral associations at the lower levels of ore veins for the low-temperature ones at the upper levels, and reversed, when high-temperature associations at lower horizons appear to be substituted by high-temperature associations in the upper part of the deposit (Bukuka).

The plutonogenic hydrothermal deposits are formed at the same depth as the greisen tungsten deposits (5-1 km), quartz-wolframite veins being though localized somewhat higher than the greisens. The following ore formations are distinguished: (1) quartz-wolframite (Antonovogorskii in Transbaikal region); (2) quartz-hübnerite (Bom-Gorkhon in Transbaikal region); (3) cassiterite-wolframite (Iultin in Chukotka, Panasqueira in Portugal); (4) quartz-scheelite (Boguty in Kazakhstan); (5) quartz-sulfide-wolframite-hübnerite (Bukuka, Kholtoson, Inkur in Transbaikal region).
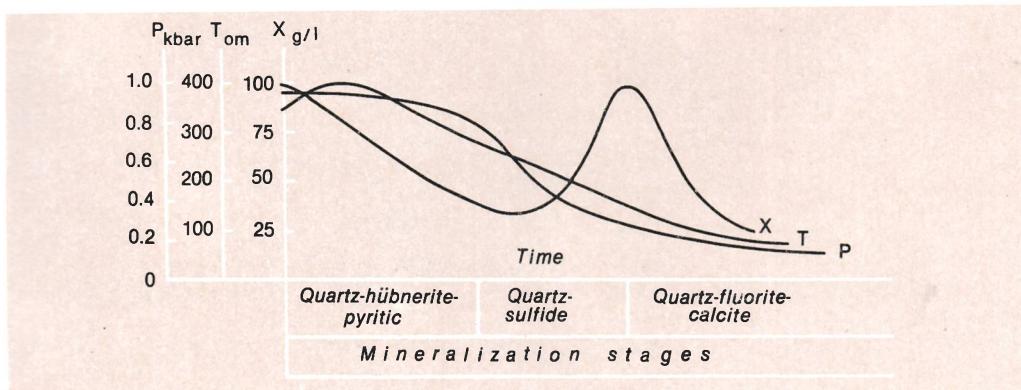
Fig. 78. P-T-X conditions of the formation of Bom-Gorkhon deposit. (After E. Polyanskii)

*Deposits of Quartz-wolframite
and Quartz-hübnerite Formation*

BOM-GORKHON DEPOSIT is located in western Transbaikal region. It is confined to the Bom-Gorkhon granitoid massif of the Upper Jurassic age (160-175 m.y.) which was emplaced in two phases: (1) early phase involving the intrusion of diorite and porphyry-like biotite granites (the temperature of crystallization is 1 020-930 °C, the pressure being 1.5-1.3 kbar); (2) late phase consisting in the intrusion of leucocratic granites (1 050-950 °C, the pressure being 1.5-1.3 kbar). Granites are cut by dikes of aplite-like granites, granite-porphyries and pegmatites (720-500 °C, the pressure being 1.02-0.96 kbar).

The ore bodies are represented by quartz-hübnerite veins (Fig. 77) confined to a system of conjugated prototectonic fissures of the NE and NW strike, gently dipping (15-30°) to south-east and north-west. These fissures appeared during the emplacement of porphyry-like granite of phase I, and that is why they develop only in this variety. The largest vein is traced to the depth of 800 m. Its thickness varies from 0.1 m to 3 m in swells which are observed at the places of fissure conjugation. The veins exhibit an intricate branching pattern and have numerous apophyses.

The main ore mineral is hübnerite, the gangue mineral – quartz; the subordinate minerals: scheelite, molybdenite, pyrite, chalcopyrite, sphalerite and cosalite as well

as fluorite and calcite. The ores are characterized by banded, drusy and disseminated structures and by hypidiomorphic, radial and corrosion textures. Also observed is the texture of mutual boundaries. The alteration of the host granites consists in greisenization. According to Ph. Melnikov and E. Polyansky (Fig. 78) three mineral associations were segregated successively in a single process of mineral formation: quartz-hübnerite-pyrite (at the temperature of 395-255 °C and pressure of 0.96-0.80 kbar), quartz-sulfide (270-180 °C and 0.6-0.3 kbar) and quartz-fluorite-calcite (100-80 °C and 0.1 kbar). Hydrothermal solutions are also found to change their concentration from 100 to 10 gr/l and less (Fig. 78). The detected temperature zonality is indicative of the direction in which the fluids move along the ascending ore-localizing fissures, and this is reflected in the vertical mineral zonality: quartz-hübnerite-pyrite association is developed at lower levels, quartz-sulfide one – at the intermediate levels, whereas quartz-fluorite-calcite association – at the upper ones.

*Deposits of Quartz-cassiterite-
wolframite Formation*

PANASQUEIRA DEPOSIT is situated in Portugal. The deposit area is composed of the Upper Proterozoic-Lower Paleozoic sequence of sandy shales. The latter is crumpled into gentle folds complicated by pre-ore downthrow faults and intruded by the Hercynian granite massif. At its exocontact zone the host rocks are altered
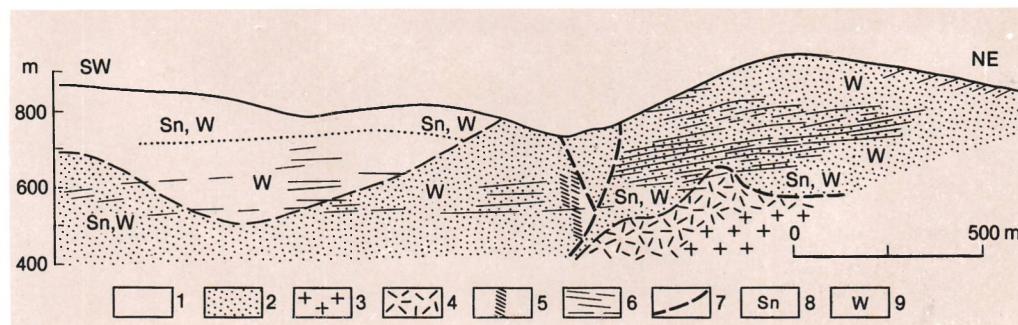
Fig. 79. Schematic geological section through the Panasqueira tungsten-tin deposit. (After D. Tadeu)

1 – sandy-shale sequence of Upper Proterozoic-Lower
    Paleozoic;
2 – sandy-shale sequence altered at the contact with
    granite into biotite-cordierite hornfels;
3 – granites;
4 – greisenized granites;

5 – dolerite dikes;
6 – ore veins;
7 – downthrow fault;
8 – zone of tungsten ores;
9 – zone of tin-tungsten ores

into chlorite-biotite and cordierite hornfels. The dome-like uplift of the massif constituted by leucocratic muscovite granite-porphyry of the hypabyssal facies is exposed by subsurface mining workings at a depth of 300 m from the surface.

The ore bodies are represented by a series of gently dipping quartz-wolframite veins localized in hornfels parallel to the roof of the massif and occasionally penetrating the granites (Fig. 79). They fill in the contraction fissures of detachment, forming systems of veins and subhorizontal lenses of the total extension up to 8 km, the width being up to 800 m. The size of individual ore bodies is tens-hundreds of metres across, the average thickness being 0.3-0.5 m (2-3 m in swells).

The main ore minerals include wolframite and cassiterite; the subordinate ones – arsenopyrite, antimonite, chalcopyrite and pyrite; the gangue minerals are represented by quartz, topaz, muscovite, siderite, calcite. The ore is characterized by banded, massive and drusy structures and by crystalline, radial and corrosion textures as well as by the texture of mutual boundaries. The hydrothermal alteration of the host hornfels is expressed in tourmalinization, silicification and sericitization. The following stages of the mineral formation are distinguished: (1) tourmaline-topaz one with cassiterite; (2) quartz-wolframite stage; (3) sulfide stage; and, (4) the final quartz-carbonate stage. The early ore associations, according to

A. Clarke, were deposited at high temperatures (610-490 °C), the pressure being 1 000-500 bar. The zonality is expressed by the fact that wolframite is predominant in the central parts of the vein clusters whereas mixed wolframite-cassiterite ores are observed in the periphery (in the upper and lower parts and on the flanks).

*Deposits of
Quartz-scheelite Formation ·*

BOGUTY DEPOSIT is situated in Kazakhstan. The deposit area is composed of the sandy-shaly sequence of the Middle Ordovician age which forms an anticline and is intruded by the Caledonian Boguty massif of fine-grained leucocratic granite. Its south-eastern exocontact is complicated by a zone of intense foliation that controls the mineralization.

The ore body is represented by a stockwork zone traceable for 1 600 m along the strike of using thickness. The zone comprises quartz veins first metres-tens of metres long (rarely up to 150-200 m) and 0.1-0.7 m thick, and numerous veinlets observed as a dense network, especially in sandstones and granites (Fig. 80). They strike almost from north to south and dip in the western direction, towards the plunge of the roof of the massif.

The main ore minerals are pyrite and scheelite; the gangue minerals include quartz and muscovite; wolframite, molybdenite, chalcopyrite and galena as well as
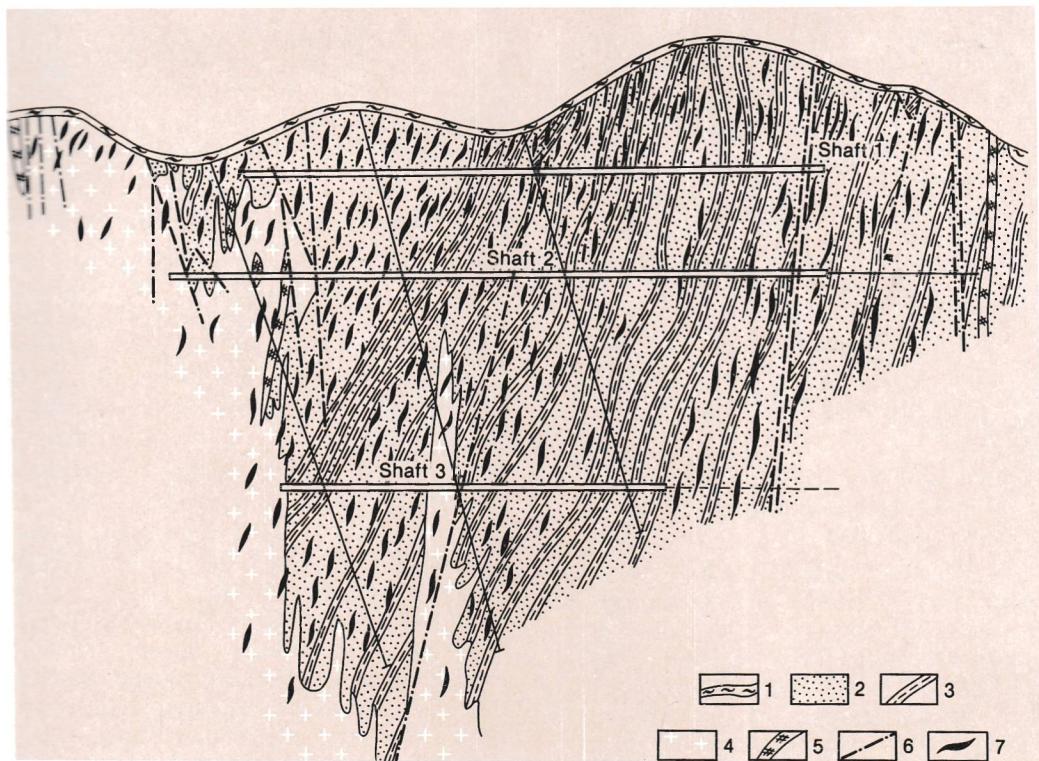
Fig. 80. Schematic geological section through the Boguty deposit. (After A. Shcheglov and T. Butkevich):

1 – deluvium;
2 – sandstones;
3 – schists;
4 – granites;

5 – lamprophyre dikes;
6 – faults;
7 – quartz-scheelite veins and veinlets

tourmaline, fluorite and K-feldspar are subordinate. The host rocks are hydrothermally altered into chlorite-sericite-quartz rocks and also strongly tourmalinized and fluoritized.

Deposits of Quartz-sulfide-wolframite-hübnerite Formation

The deposits of this formation, as compared to the deposits of quartz-wolframite and quartz-hübnerite formations, are characterized by the enrichment of the ores with sulfides (pyrite, galena, sphalerite and chalcopyrite).

VOLCANOGENIC HYDROTHERMAL DEPOSITS

Volcanogenic hydrothermal tungsten deposits containing complex ores (Sn – Ag – W,

Hg – Sb – W, Au – W, Mn – W) are known in the USSR in Transbaikal region (Barun-Shiveya, Novo-Ivanovskii), Central Asia (Tasor, Ikar) and in the Caucasus (Zopkhito); abroad: in China (Usin, Siang), Japan (Akenobe, Asyo), Turkey (Gyumyusler), Canada (Tungoten-Queen), the USA (Yellow, Boulder, Atolia), Bolivia (Ascension, Tasna), Peru (Morokocha) and Australia (Hillgrow). These deposits are located in the areas of recent and young volcanism accompanied by thermal springs. They are deposited in the subvolcanic, shallow and surface environments. The deposits are associated with andesite-dacite-rhyolite formations, with volcanics of relatively high alkalinity. They are usually confined to the formations of extrusive, vent and subvolcanic facies,

occasionally they occur among tuffaceous and sedimentary rocks. Volcanic domes, necks and synvolcanic zones of crush and jointing serve as ore-bearing structures. The ores occur as stockworks and veins showing a complex branching patterns and rarely as concordant lenticular bodies. The veins are small in size: they are traceable for tens-hundreds of metres along the strike and up to 250-300 m, occasionally up to 600-700 m along the dip, the thickness being 0.1 up to 5 m (up to 10 m in swells).

Three ore formations are distinguished: (1) (cinnabar)-antimonite-scheelite-ferberite; (2) silver-gold-scheelite; (3) psilomelane-tungomelane.

Deposits of (Cinnabar)-antimonite-scheelite-ferberite Formation

Ferberite, scheelite and actinolite, occasionally cinnabar are the main ore minerals; arsenopyrite, gudmundite, pyrite, marcasite, chalcopyrite, sphalerite, galena, tetrahedrite, hematite are subordinate. The main gangue minerals are quartz and chalcedony; the subordinate gangue minerals consist of fluorite, barite, dickite, sericite, ankerite and calcite. Hydrothermal alterations of the host rocks manifest themselves in silicification, sericitization, adularization and argillization.

Several stages of mineral formation are identified, the main ones among which are the following: (1) pyrite-arsenopyrite; (2) ferberite-scheelite; (3) antimonite-cinnabar; (4) post-ore carbonate. The temperature interval of mineral formation is 350-70 °C. Thus, in the Transcaucasian deposits (Mountainous Racha, Zopkhito), according to V. Naumov and G. Ivanov, ferberite was segregated at 310-270 °C, quartz – at 250-200 °C and antimonite – at 80-70 °C. The ore deposition, for example at the Atolia deposit (USA), occurred at a depth not exceeding 200-300 m.

Deposits of Silver-gold-scheelite Formation

With respect to the tungsten ore, these are small targets, formed in approximately the same conditions as are the deposits of the (cinnabar)-antimonite-scheelite-ferberite

formation. Thus, for instance, the Boulder deposit (USA), according to G. Lovering and O. Tweto, was formed at 300-200 °C, the pressure being less than 100 kgf/cm^2; the deposit is associated with dikes of the basic rocks, differentiates of the basaltoid magma.

Deposits of Psilomelane-tungomelane Formation

Minor deposits of manganese-tungsten ores occurring among travertines (Tasor in the Central Asia, Golconda in the USA) are the product of the recent thermal springs activity. They are represented by sheet bodies composed of psilomelane, limonite and tungomelane.

PLACER DEPOSITS

Placer tungsten deposits are known in the USSR in the Magadan area (Iultin), Yakutia (Omchikandin), Transbaikal region (Sherl Mountain), Kazakhstan (Kara-Oba, Boguty); abroad in China, Burma (Bvabin, Heida), Indonesia, Thailand, Congo, Bolivia, the USA (Atolia in California). They are closely related to primary ore deposits and therefore are frequently mined together with the latter. Their formation is mainly due to disintegration of greisen and especially plutonogenic hydrothermal ore deposits of quartz-cassiterite-wolframite, quartz-wolframite, quartz-hübnerite and quartz-scheelite formations. Most widespread are cassiterite-wolframite and volframite placers, hübnerite and scheelite ones are less distributed. Complex placers contain 0.3 up to 20 kg/m^3 wolframite. Predominantly eluvial and alluvial placers up to 5 km long are common among them.

14 MOLYBDENUM DEPOSITS

Molybdenum was discovered by K. Sheele in 1778, but has been in usage only in the 19th century. Metallurgy is the main sphere of its application (85-90%) in which it is part of alloyed steels and alloys with V, W, Cu, Ni and Co (stellite) as well as with C (carbide). Apart from this molybdenum has a wide application in electrical and thermal engineering, chemical and oil-refin-

ing industries, and is used as an admixture in fertilizers. Molybdenum is obtained from the molybdenum, tungsten-molybdenum, copper-molybdenum and uranium-molybdenum ores.

The price of one ton of molybdenum in concentrate is as much as 3 800 US dollars. In 1975 in the capitalist and developing countries a total of 70 300 tons of molybdenum concentrate were produced; molybdenum reserves make up as follows: 5.4 million tons of prospected and 8.4 million tons of total reserves. Unique deposits (Climax, Henderson in the USA) contain over 500 000 tons of metal; very large and large deposits – 500 000-100 000 and 100 000-50 000 tons, respectively; average and minor deposits – 50 000-25 000 tons and less than 25 000 tons, respectively. High-grade ores contain over 0.5% Mo, ordinary ores – 0.5-0.2% Mo, low-grade ores – 0.2-0.1 Mo, and very low-grade complex ores – 0.1-0.02% Mo.

GEOCHEMISTRY AND MINERALOGY

There are seven stable molybdenum isotopes with the mass number of 92, 94-98, 100, the ^{98}Mo (23.75%) being predominant. The metal has two valencies: four-valent in endogenous conditions and six-valent in an exogenous environment. Molybdenum crustal abundance (clarke) is $1.1 \cdot 10^{-4}$%, its concentration coefficient being 5 000. The abundance of molybdenum increases from low to high siliceous rocks, making up $2 \cdot 10^{-5}$ for ultrabasites and $2 \cdot 10^{-4}$% for granites. Accordingly, molybdenum is geochemically associated with the acid alkali-earth magma, which determines its concentration at post-magmatic stages from hydrothermal solutions.

Under endogenous conditions molybdenum is transported in the form of complex compounds (heteropolysilicic acids of $SiO_2 \cdot 12MoO_3 \cdot nNa_2O \cdot H_2O$ types) in acid or weakly acid solutions at a pressure of 600 kgf/cm^2 and temperature 600 °C. With a temperature decrease, this complex disintegrates, and in the presence of hydrogen sulfide it disassociates to form molybdenite and to produce silicification of host rocks.

Under exogenous conditions molybdenite is oxidized forming easily soluble compounds of the $MoSiO_2$ and H_2MoO_4 type. In pyrite-bearing ores they form ferrimolybdenite, in carbonate ores – powellite or migrate in surface water solutions, being partially bound as molybdenoorganic compounds of oilbitumens, coals, carbonaceous and coalysiliceous shales.

Molybdenite MoS_2 with an isomorphic admixture of Re is the main mineral of molybdenum ores; molybdescheelite $Ca(Mo, W)O_4$ (0.5-15%), known from some skarn deposits, is subordinate, while powellite $CaMoO_4$ (48%), ferrimolybdite $Fe_2O_3 \cdot 2MoO_3 \cdot 7H_2O$ (60%) and wulfenite $PbMoO_4$ (46%) originating in an oxidation zone, play a very negligible role.

METALLOGENY

Endogenous molybdenum deposits solely belong to post-magmatic granite magma formations. They developed at the middle and especially at the late stages of a geosynclinal cycle, as well as due to the magmatic reactivation of the platform cycle. According to V. Pokalov (1972), copper-molybdenum deposits are associated with monzonite, granodiorite and granosyenite; monometal molybdenum deposits are related to normal biotite-hornblende granite, while tungsten-molybdenum deposits – to leucocratic subalkaline varieties. Distribution of the massifs of such ore-productive granitoids and associated molybdenum deposits is controlled by major faults.

Exogenous molybdenum-bearing coals, coaly and coaly-siliceous shales were formed at the early stage of a geosynclinal cycle and in platform conditions. Though they have sufficiently large resources, these deposits are considered to be the distant future targets due to the low molybdenum content (thousandth-hundredth fractions of a per cent).

A tendency toward an increase in the number of molybdenum deposits from old to young epochs is noted in the geological history of the earth crust. Some sporadic

molybdenum hydrothermal deposits are known to form in the Archean and Proterozoic epochs (La Corn in Canada; Qnaben in Norway). Their number increased in the Caledonian time (Sora in Kuznetsk Alatau; Mesters Wig in Greenland), especially in the Hercynian epoch (Eastern Kounrad, Koktenkol in Kazakhstan; Azfour in Morocco). Major molybdenum deposits are associated with the Kimmerian and Alpine epochs (Bugdaya, Shakhtama in Transbaikal region; Turnyauz, Kadjaran in the Caucasus; Tzynduichan in China; Climax in the USA; Endako in Canada).

TYPES OF COMMERCIAL DEPOSITS

The following types of commercial molybdenum deposits are recognized: (1) skarn; (2) greisen; (3) plutonogenic hydrothermal; (4) volcanogenic hydrothermal.

SKARN DEPOSITS

The Turnyauz deposit in the Northern Caucasus is the most representative of this type in the Soviet Union. Skarn deposits are also known in Kazakhstan (Karatas I) and in Khakasiya (Kiyalykh-Uzen); and in other countries – in Roumania (Baja), China (Yantzy-Chshantzy), Morocco (Azfour), the USA (Pine Creek), Brazil (Quinkhaba), Turkey (Takhtalydag). The skarn deposits are confined to calcareous skarns developed at the contact between granitoids or other alumosilicate rocks and carbonates.

Ore bodies have a sheet-like, lens-like, vein, or a more complex shape, being represented occasionally by stockworks of the stringer-type ores in granitoids and hornfels. Molybdenite and pyrite as well as scheelite (or molybdoscheelite), chalcopyrite and magnetite are the main ore minerals; sphalerite, galena and grey ore are subordinate; native bismuth, native silver and gold are rare. Skarn minerals include garnet of a grossularite-andradite series, pyroxene of hedenbergite-salite-diopside series, plagioclase, epidote and vesuvianite; gangue minerals are represented by quartz,

muscovite, chlorite, fluorite and carbonate. Sulfide mineralization superimposed on skarns is accompanied by feldspar-quartz metasomatites. Ore deposition involves several stages in the temperature range from 500 to 200 °C. The initial stages concluding the formation of skarns are enriched in scheelite, intermediate stages – in molybdenite, and later ones, in sulfides of base metals, chalcopyrite in particular.

Two ore formations are recognized in these deposits: scheelite-molybdenite (Turnyauz) and chalcopyrite-magnetite-molybdenite (Karatas I, Kiyalakh-Uzen).

Deposits of Scheelite-molybdenum Formation

TURNYAUZ DEPOSIT is situated in the Northern Caucasus and is confined to the intersection of a sublatitudinal fault zone with a transverse uplift. The area of the deposit is a fragment of a major fold structure composed of highly dislocated and contact-metamorphosed carbonate terrigenous and volcanogenous rocks of the Middle Paleozoic age. Neointrusions represented by leucocratic granitoids (20-18 m.y.), porphyric granites (1.9-1.8 m.y.) and volcanogenic liparites (1.8-1.6 m.y.) are developed within the area. Reef limestones make up the core of a fault-related anticline overlain by hornfelsed shales and sandstones whose contacts are complicated by shear zones.

The main ore body has a shape of a saddle and is composed of skarns with scheelite and molybdenite occurring at the contact between limestones and hornfels at the hinge of the anticline, where it is up to 200 m thick (Fig. 81). Thick skarn bodies were formed at the expense of limestones and hornfels. At the contact between granitoids and limestones skarns occur only as thin fringes. Quartz-molybdenite mineralization of the stringer-disseminated type, known to occur at flanks of the deposit, forms stockworks within skarn bodies as well as in marbles and leucocratic granitoids.

Scheelite, molybdoscheelite and molybdenite are the main ore minerals; magnetite, pyrrhotite, chalcopyrite, sphalerite and bismuthinite are subordinate;
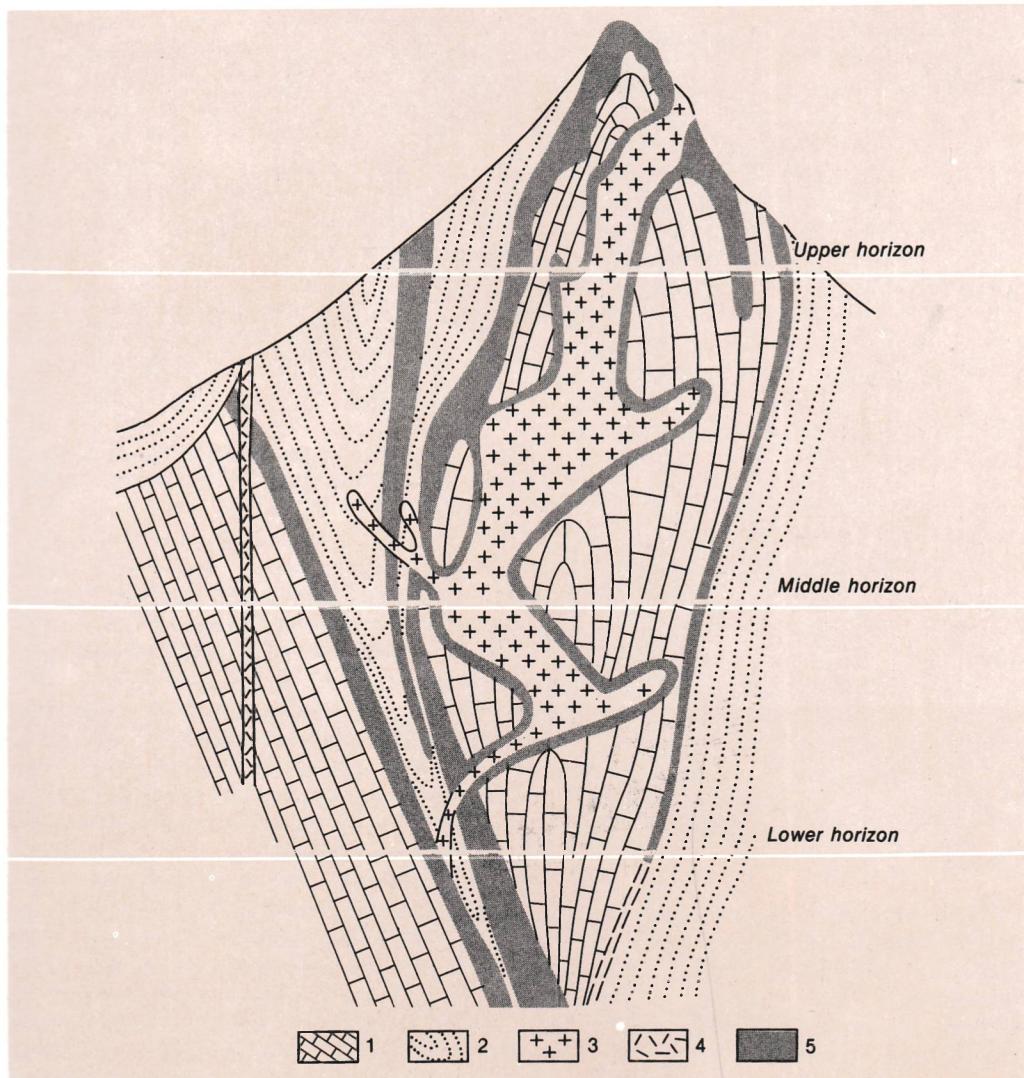
Fig. 81. Schematic geological section through the Tyrnyauz deposit. (After A. Pek, interpretation of √. Smirnov):

' – limestones, marmorized;
: – biotite hornfels;
3 – leucocratic granites;

4 – liparites;
5 – skarns

garnet, pyroxene, plagioclase, wollastonite, vesuvian, quartz, calcite and fluorite are gangue minerals. Ore structures are massive, brecciated, mottled with pockets and stringer-disseminated; textures are granoblastic and crustified. Scheelite and molybdoscheelite commonly occur as irregular fine impregnation and 1-2-cm-thick stringers. Molybdenite forms thin-flaky aggregates, flakes and stringers.

According to O. Kononov and E. Gramenitskii, four stages in formation of ore mineralization can be distinguished: (1) skarn (650-380 °C), followed by intrusion of leucocratic granitoids; (2) postskarn metasomatites with molybdoscheelite, scheelite and molybdenite (500-200 °C); (3) quartz-molybdenite (400-180 °C) followed by Eljurt granite intrusion; (4) magnetite-sul-

fide-scheelite (275-80 °C) concluded in formation of liparite.

There is a vertical zonation which manifests itself in the decrease with depth of the amount of molybdenite and scheelite, which are substituted by molybdoscheelite with the increased Mo^{6+} content. Horizontal zonality consists in the decrease of Mo^{6+} content in molybdoscheelite from the centre of an ore body towards its flanks.

The deposit was formed in the Late Alpine epoch of tectonic and magmatic reactivation along the margin of the Scythian Platform and is associated with neointrusions which developed during 20 million years.

Deposits of the Chalcopyrite-magnetite-molybdenite Formation

Calcareous skarns composing the deposits of this formation contain magnetite that is associated with skarn minerals, as well as with quartz, chalcopyrite and molybdenite which formed later mainly in quartz-sulfide veinlets. Chalcopyrite-quartz assemblage develops mainly in iron-rich skarns, while molybdenite-quartz one, in granitoids and hornfels.

GREISEN DEPOSITS

Molybdenum, often tungsten-molybdenum, greisen deposits are known in the Soviet Union in Transbaikal region (Buluktai, Pervomaiskii) and Central Kazakhstan (Eastern Kounrad, Akchatau, Janet, Koktenkol), and abroad – in Mongolia (Yugodzyr), Argentina (Cerro-Aspero). They are restricted to the liparite granitic cupolas extending in them for 300-500 m, and in the overlying hornfels – for up to 1 200-1 500 m. Ore-bearing greisens occupy faults, fractures of the linear and ring types, and cleavage structures.

Ore bodies occur as veins, stockworks and stocks, in places having a pipe-like shape. Greisens consist of mica (muscovite, biotite) and quartz as well as of sodic plagioclase, microcline, tourmaline, topaz, fluorite. Main ore minerals include molybdenite and wolframite, while bismuth, cassiterite, magnetite, pyrite, chalcopyrite, sphalerite and galena are subordinate.
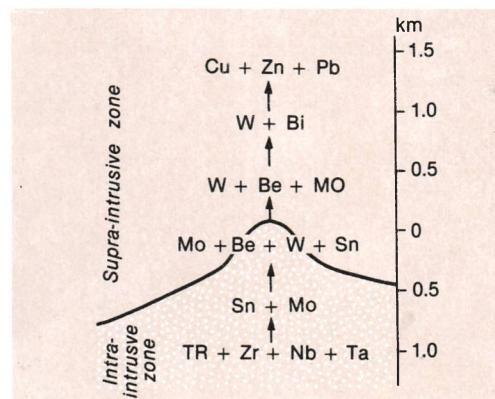
Fig. 82. Scheme showing distribution of complex ore during the formation of greisen deposits. (After G. Shcherba)

The ore emplacement took a long period of time, was intermittent and synchronous with the formation of ore-controlling structures. Metasomatic type of ore emplacement was succeeded by the filling of fractures. The main stages of ore formation are as follows: (1) the early and late greisen; (2) the stage of quartz and quartz-feldspar vein; (3) sulfide; (4) post-ore quartz-carbonate. The first three stages are most productive for molybdenum and tungsten mineralization. As it is shown by decrepitation of fluid inclusions, greisenization of the ores in Kazakhstan occurred in the range of 470-360 °C, while crystallization of vein ore containing quartz took place in the range of 540 to 300 °C. A vertical zonality distinctly manifested in greisen deposits is expressed in development of rare-earth, zirconium and tantal-niobium mineralization in the lower parts, molybdenum-tin-tungsten – in the intermediate, and lead-zinc-copper – in the upper parts of the ore deposits (Fig. 82).

Greisen molybdenum-tungsten deposits were formed in orogenic zones and in reactivation regions at a depth varying from 5 to 1 km.

EASTERN KOUNRAD DEPOSIT is located in Kazakhstan within the Permian massif composed of leucocratic granite (262 ± 10 m. y.) of the same name. The massif is cut by veins of fine-crystalline granites and aplites, dikes of diorite porphyries and gabbroporphyries and by a large NW-trending

fault, east of which fine-crystalline granites of endocontact facies with xenoliths of host rocks, with numerous dikes, greisen bodies and quartz veins are developed. The prevailing systems of vein fractures trending sublatitudinally are complicated by feathering fissures of other directions. A quartz-molybdenite vein, as well as the molybdenite-bearing near-vein and intravein greisens compose the ore body. The greisens form symmetrical zones along both walls of the vein and gradually pass into granites.

Steeply dipping ore veins form an echelon pattern, each vein being 250 m in length. The veins constitute a vein system, i.e. the main ore zone trending sublatitudinally and totalling 8 km in length. The veins pinch out at depths from 200 to 300 m from the surface. Molybdenite and pyrite are the main ore minerals; quartz, muscovite and fluorite are gangue minerals; chalcopyrite and ilmenorutile as well as albite and microcline are subordinate; wolframite, magnetite, sphalerite are rare. Quartz is the main mineral of the greisens; less important are muscovite and plagioclase. Also occur biotite, garnet, fluorite, sphene, magnetite, hematite, ilmenorutile, zircon and topaz as well as pyrite and molybdenite. In quartz veins (commonly at vein salbands) molybdenite occurs as large, platy, rosette-like and spherolite segregations, while in greisens it is developed as a fine irregular impregnations. Hypergene minerals of an oxidation zone (first tens of metres) include powellite, limonite, jarosite and covellite, and also gypsum, halloysite, montmorillonite and opal.

Three stages of mineral formation are recognized: (1) formation of molybdenum-bearing greisens and quartz veins in which molybdenite, pyrite, quartz, hematite and magnetite were successively emplaced (the productive phase); (2) formation of banded quartz veinlets containing tungsten mineralization; (3) filling of veins and veinlets with white drusy quartz.

A vertical zonality manifests itself in a change (from bottom to top) of three zones (Fig. 83): (1) a supra-ore zone represented by quartz veins and near-ore quartz-muscovite and muscovite greisens
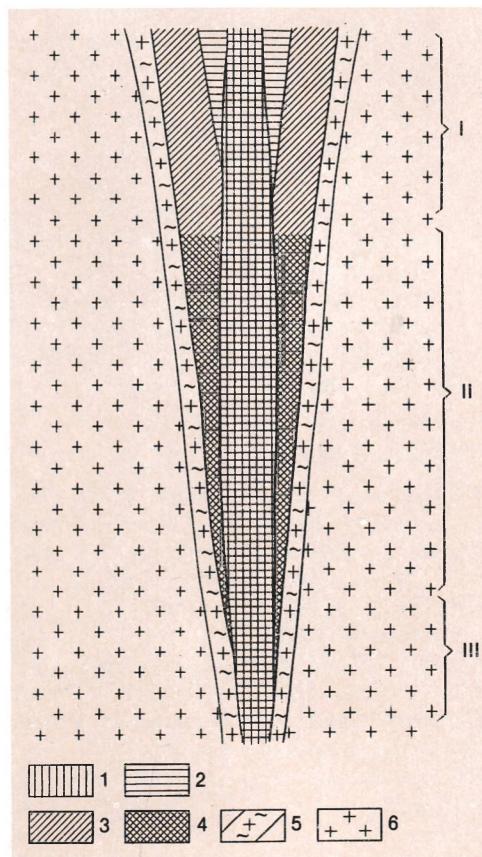
Fig. 83. Zonality of wall-rock alterations at the Eastern Kounrad deposit in the vertical transverse section. (After V. Pokalov):

1 – quartz vein filling;
2 – muscovite greisen;
3 – quartz greisen;
4 – quartz-muscovite greisen;
5 – altered granite;
6 – granite.
Zones:
I – supra-ore; II – ore;
III – sub-ore
Note: a ratio of vertical scale to horisontal one is 1:40

with low-grade molybdenum and tungsten mineralization; (2) an ore zone to which commercial grade ores both in quartz veins and near-vein quartz greisens are confined; (3) a sub-ore zone in which quartz greisens pinch out, while the thickness of quartz veins decreases; its molybdenum content is below the commercial grade. The horizontal zonality is expressed in substitution, from west to east along the strike, of ore-rich

veins by ordinary and then low-grade ores, which is due to the tilt of the ore zone in the same direction (F. Chukhrov, 1960).

PLUTONOGENIC HYDROTHERMAL DEPOSITS

These are the most abundant among molybdenum deposits and are of a first-rate practical importance. Three main ore formations are distinguished in the group: (1) quartz-molybdenite; (2) quartz-molybdenite-sericite; (3) quartz-molybdenite-chalcopyrite-sericite.

Deposits of the Quartz-molybdenite Formation

These deposits are widespread in the Soviet Far East (Umalta), Transbaikal region (Bugdaya, Zhireken, Davenda, Shakhtama), Mountainous Altai (Kalguty) and Kazakhstan (Shalgiya); and in other countries: in Norway (Qnaben), the USA (Questa I) and Canada (Boss-Mountain). They are associated with halos of biotite-hornblende and biotite-muscovite granites. Ore bodies commonly confined to late acid and subalkaline dikes occur as veins and stockworks.

The main ore minerals include molybdenite, in places with wolframite; subordinate minerals are represented by cassiterite, scheelite, pyrite, arsenopyrite, pyrrhotite, bismuthinite, chalcopyrite sphalerite and galena; the main gangue minerals include quartz, potassium feldspar and plagioclase, while muscovite, tourmaline, fluorite and carbonates are subordinate.

Ore formation process involved several stages: (1) pre-ore quartz-tourmaline; (2) early quartz-molybdenite; (3) late quartz-wolframite-molybdenite; (4) sulfide; (5) post-ore fluorite-chalcedony-carbonate. Enclosing granites are transformed into feldspar and quartz-feldspar metasomatites or greisens. Vertical zonality commonly consists of subsitution, from top downwards, of molybdenum mineralization by tungsten-molybdenum one, and then, locally, by polymetallic mineralization. The concentric zonal pattern, in which early and high-temperature barren quartz mineralization occurs in the centre, and the later and lower temperature ores represented first by molybdenum and second by base metal ore in the periphery is observed in case of a stockwork type of mineralization.

SHAKHTAMA DEPOSIT is located in the Eastern Transbaikal region. The area is composed of Jurassic biotite-hornblende granite and granodiorite accompanied by eruptive breccias. The rocks are cut by a belt of Upper Jurassic lamprophyre diorite-porphyry and granite-porphyry dikes of the sublatitudinal and north-western strikes (Fig. 84). The deposit consists of sublatitudinally trending quartz-molybdenite veins arranged in an echelon manner. Low-grade ore stockworks are located between them. The veins cut the dikes at an acute angle, gradually pinching out inside in the form of veinlets. In places, they are confined to the dike contacts. The ore bodies extend down to 300 m from the surface. The internal structure of the veins is complex, which is due to the repeated opening of up-throw and strike-slip faults to which these veins are confined.

The main ore mineral is molybdenite of two generations – large-flaky I and fine-flaky II; subordinate minerals include pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, grey ores, antimonite, scheelite. Quartz is the main gangue mineral; dolomite, calcite, fluorite are subordinate. Structures are banded and brecciated.

Several stages are recognized in the ore formation process: (1) pre-ore, involving quartz-tourmaline and quartz-molybdenite veinlets; (2) early quartz-molybdenite; (3) late quartz-molybdenite; (4) final sulfide; (5) post-ore carbonate. The enclosing granites are hydrothermally altered: K-feldspathized, sericitized, berezitized and agrillitized.

Deposits of Quartz-molybdenite-sericite and Quartz-molybdenite-chalcopyrite-sericite Formations

These are represented by large molybdenum, often copper-molybdenum stringer-disseminated deposits. In the USSR they are known in the Trans-Caucasus (Kadjaran), Kuznetsk Alatau (Sora); in other countries:
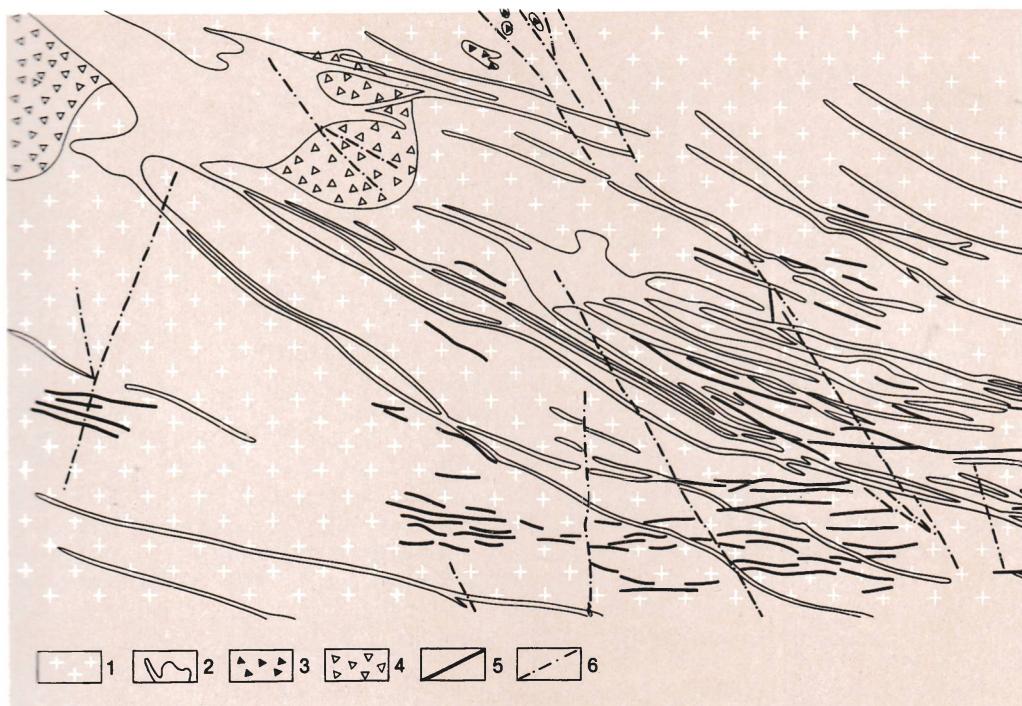
Fig. 84. Schematic geological map of the Shakhtama deposit (based on the data of Shakhtama Geological Prospecting Team):

1 – granites and granosyenites;
2 – Late Jurassic dikes of lamprophyres, diorite porphyrites, granodiorite-porphyries and granite-porphyries;

3 – eruptive breccias;
4 – biotitized breccias of granite;
5 – quartz ore veins;
6 – faults

in China (Tzynduichan), the USA (Climax, Henderson), Canada (Endaco, Betlekhem). The deposits are related to porphyry intrusions of diorite-granodiorite-granite complexes of potassium and potassium-sodium series which are members of volcano-plutonic associations. These deposits are localized in the endocontact zones of intrusive bodies or at their outer contact (exocontact) zone; they are confined to stocks and dikes of granite-porphyry, granodiorite-porphyry, syenite-porphyry and monzonite-porphyry, and are controlled by faults, being located at points of their intersection.

Ores occur as concentric or linear stockworks and belong to molybdenum-porphyry and copper-molybdenum-porphyry formations. Predominant (80-90%) among them are quartz-molybdenite and quartz-sulfide veinlets varying in thickness from 1-2 to 2-3 cm; dissemination and pockets of sul-

fides, less frequently, sulfide-quartz veins, are also observed. Concentric stockworks are hundreds of metres to some kilometres across, the linear stockworks are traceable for first kilometres, the width being a few hundred of metres. The main minerals of the primary ores include molybdenite (locally chalcopyrite) and pyrite; subordinate – magnetite, hematite, bornite, grey ores, galena and sphalerite; the main gangue minerals are quartz and sericite; subordinate are feldspar, epidote, chlorite and carbonate. The average molybdenum content varies from 0.05 to 0.5% for molybdenum-porphyry deposits, and from 0.005 to 0.25% for copper-molybdenum-porphyry ones.

The mineral formation took a multi-stage pattern. For example, formation of copper-molybdenum deposits in Armenia, according to S. Movsesyan and M. Isaenko (1974), proceeded in seven stages, each characterized by changing paragenetic associa-

tions of minerals having their own deposition temperatures, namely: (1) pyrite; (2) quartz and quartz-magnetite (450-400 °C); (3) molybdenite and molybdenite-quartz (320-280 °C); (4) quartz-pyrite and tennantite-enargite (230-190 °C); (5) quartz-galena-sphalerite; (6) dolomite and dolomite-chalcedony (150-110 °C); (7) anhydrite-gypsum (110-80 °C). As is indicated by thermometric studies performed for other similar deposits in the USSR, the pre-ore K-feldspar metasomatites were formed in the range of 700-400 °C, the early barren quartz veins at a temperature interval of 470-390 °C, while productive quartz-sulfide assemblages developed at 400-200 °C. Host rocks underwent significant hydrothermal alterations: K-feldspathization, silicification, sericitization, argillization, propylitization. The metasomatites and ore mineralization are characterized by the vertical and horizontal zonalities, frequently concentric (see Fig. 51).

The deposits were emplaced at a depth of 1-2 km from the surface. A deep, probably mantle source is assumed for sulfide sulfur, as the $\delta^{34}S$ is close to meteoritic, and $^{87}Sr/^{86}Sr$ is close to basaltic.

CLIMAX DEPOSIT is located in the USA (Colorado State) and represents a quartz-molybdenite-sericite formation. Molybdenum reserves are estimated at 825 000 tons, the content being 0.2%. The area is composed of Precambrian granites, gneisses and crystalline schists. In the west, along the Mosquito Fault having an amplitude of 2 700 m they are brought into contact with Paleozoic sediments. All the rocks are intruded by pre-ore stocks and dykes of the Paleogene porphyry rocks. Within the deposit there is the complex Climax stock essentially composed of quartz monzonite-porphyry. It is pipe-like in shape and 1 km across. The stock intrudes Precambrian

rocks; its formation involved four phases, each accompanied by dykes and hydrothermal mineralization.

The ores of the Climax deposit occur as stockworks essentially composed of quartz-molybdenite veinlets (97% of molybdenum resources) traced both in Precambrian rocks (60%) and in the porphyries (40%). These veinlets are restricted to local zones of fracturing genetically associated with the porphyric stock. The deposit is represented by three ore bodies (from top downwards): Sirisco, almost completely eroded, Upper and Lower bodies, spatially and genetically related to the first three phases of formation of the Climax stock. All the three bodies possess a similar shape, structure, mineral composition and ore zonality; they occur at the roof above the porphyric intrusion of the corresponding phase of emplacement.

The Upper ore body is the largest and best studied. In plan it is circular, in section, arch-shaped (Fig. 85). The average thickness of the ring is 250 m, the inner diameter is 210 m; the ore body has been traced to a depth of 800 m. The main ore minerals include pyrite, molybdenite; gangue minerals are represented by quartz and sericite; chalcopyrite, wolframite, cassiterite and sphalerite as well as topaz, calcite and rhodochrosite are subordinate. Typomorphic ore structures are stringer, textures are metagranular. There is only a weak oxidation zone. W, Sn, RE and Th (in monazite) are also extracted apart from Mo, as by-products.

The veinlets were developed in three phases: (1) quartz-molybdenite; (2) quartz-chalcopyrite-pyrite; (3) quartz-sericite. Formation of ore mineralization took place in the temperature range of 400-360 °C. It was preceded by intense K-feldspathization, while strong silicification accompanied the ore deposition and also occurred after it.

Fig. 85. Schematic section through the 120th profile (*a*) and through the Philipson horizon (*b*) of the Climax deposit. (After S. Wallace):
1 – late phase of Climax Central stock;
2 – early phase of the same stock;
3 – strongly silicified rocks;
4 – the region of tungsten widespread with more than 0.02% content (a projected part is shown by a broken outline);
5 – an outline of tungsten widespread with 0.4%

content (a projected part is shown by a broken outline);
6 – faults;
7 – contacts;
8 – supposed contacts;
9 – supposed contact position in a silicified zone

(a)

Profile 16

WO₃ Zone of Upper ore body

MOS₂ zone of Upper ore body

Surface before driving the quarry

White horizon

Philipson horizon

Stork horizon

600 th horizon

929 th horizon

Southern Fault

Inner and outer portions of WO₃ zone
Inner and outer portions of MOS₂ zone

3642 m

3496

3406

3315

3214

Profile 120

(b)

Profile 120

N

WO₃ Zone of Upper ore body

MOS₂ Zone of Upper ore body

Eastern Fault

Mosquito Fault

Southern Fault

Philipson horizon

0 100 200 300 m

1
2
3
4   7
5   8
6   9

The vertical zonality is manifested in each of the ore bodies and consisted in substitution (from bottom upwards) of molybdenite by pyrite, then by hübnerite. A distinct concentric zonality is also observed. Three zones are recognized: central (from 120 to 300 m), intermediate (circular) varying in thickness from 100 to 400 m, and outer zone up to 600 m thick. The central zone is mainly composed of massive fine-grained quartz, with a weak mineralization (up to 0.1% Mo) being developed only in the margins at a great depth. Typical of the intermediate zone are quartz-molybdenite and quartz-molybdenite-orthoclase veinlets which contain 97% of the Mo reserves with 0.2-0.5% Mo. Disseminated molybdenite is found in salbands of metasomatic quartz veinlets whose thickness varies from 1 mm to 2 cm; less common are molybdenite veinlets cutting the schists. The outer zone is characterized by weak silicification and poor molybdenite mineralization but processes of sericitization and pyritization are active in it; it contains tungsten (0.06% WO_3) and tin mineralization.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

These are represented by deposits of uraninite-molybdenite formation which are discussed in the chapter "Uranium Deposits".

15 BISMUTH DEPOSITS

Bismuth was discovered in 1799 by the Swedish chemist T. Bergman. It has a wide application in alloys especially in easily fusible ones; in metallurgy it is used as an addition to stainless steel and cast iron. Bismuth is also applied in pharmaceutical, optical, electrical engineering, textile, thermonuclear and electronic industries. Only insignificant part of bismuth is obtained from bismuth ores: the 90% of its world demand is covered by bismuth recovery, as a by-product, from complex ores of Co-Ni-Bi-Ag-U, As-Bi, Cu-Bi, as well as from bismuth-bearing lead and copper ores.

The price for one ton of bismuth is 10 500 US dollars. Bismuth production in capitalist and developing countries was 4 000 tons in 1975, total reserves being 90 000 tons. Unique deposits are known in Australia (Tennant Creek). High-grade ores contain over 1% Bi, ordinary ores – 1-0.2%, and low-grade ores – less than 0.2% (in complex ores).

GEOCHEMISTRY AND MINERALOGY

Bismuth is represented by one isotope with mass number 209. Its crustal abundance (clarke) is $9 \cdot 10^{-7}\%$. Its concentration coefficient is very high: 500 000. Bismuth content increases from ultrabasic magmatic rocks $(1 \cdot 10^{-7}\%)$ to acid ones $(1 \cdot 10^{-6}\%)$. Bismuth is not concentrated in the magmatic phase. Its accumulation is related to postmagmatic processes of the granitic magma. From the magmatic sources it is transported by hydrothermal solutions in chlorine complexes $(BiCl^{2+}, BiCl^0)$ and hydrocomplexes $[Bi(OH)_3^0, Bi(OH)_2^{-1}]$.

Primary bismuth sulfide compounds are easily oxidized in exogenous processes and, passing through a sulfate phase, they are fixed in the oxidation zone in the form of oxide and carbonate compounds. In cases of weak oxidation, bismuthinite and native bismuth may be found among minerals of placer deposits.

Over 90 bismuth minerals are known, but only several of them are of commercial importance: native bismuth Bi (99.9%), bismuthinite Bi_2S_3 (81.3%), wittichenite Cu_3BiS_3 (42.15%), tetradymite Bi_2Fe_2S (59.27%), galenobismutite $PbBi_2S_4$ (55.48%), cosalite $Pb_5Bi_2S_5$ (42.10%), aikinite $CuPbBi_2S_3$ (36.29%). Bismite Bi_2O_3 (89.6%) and bismutite $BiO_2(CO_3)$ (80%) are formed in an oxidation zone.

METALLOGENY

Endogenous bismuth deposits belong to post-magmatic formations of granitic magmas. They were formed in the middle and late stages of a geosynclinal cycle as well as in relation to tectono-magmatic reactivation.

Bismuth deposits were originated during several metallogenetic epochs: Proterozoic (Eldorado in Canada), Hercynian (Adrasman in Central Asia; Yakhimov in Czechoslovakia), Kimmerian (Sangh-Dong in Southern Korea) and Alpine (Tacna in Bolivia).

TYPES OF COMMERCIAL DEPOSITS

The following types of bismuth and bismuth-bearing deposits are recognized: (1) greisen; (2) skarn; (3) plutonogenic hydrothermal; (4) volcanogenic hydrothermal.

GREISEN DEPOSITS

Greisen deposits are represented by complex ores (W-Sn-Bi) described in the chapters "Tungsten Deposits" and "Tin Deposits".

SKARN DEPOSITS

Deposits of scheelite-bearing skarns containing bismuth are described in the chapter "Tungsten Deposits".

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal bismuth deposits are known in the Soviet Union – Central Asia (Ustarasai); and in other countries – in GDR (Shneeberg), Czechoslovakia (Yakhimov), FRG (Neibulak), Peru (San Gregori), the USA (Montecristo in Arizona State) and Canada (Eldorado). They are related to granitoid intrusions. Ores mainly occur as lenses and veins. Host rock alterations in places are observed as pre-ore skarnification; hydrothermal alterations which followed ore deposition are manifested in chloritization, sericitization and silicification, in places, in hematization.

Ore formation process involved several stages: (1) arsenopyrite; (2) quartz-bismuth; (3) sulfide with bismuthinite; (4) post-ore quartz-carbonate. Zonality is indistinct, though bismuth minerals were mainly deposited in the upper levels of deposits. Among the plutonogenic hydrothermal

bismuth deposits the arsenopyrite-bismuth and penta-element (Co-Ni-Ag-Bi-U) formations are distinguished.

Deposits of the Arsenopyrite-bismuth Formation

USTARASAI DEPOSIT is located in Central Asia. The area is composed of quartzites of the Frasnian stage and a set of alternating sandstone, aleurolite, limestone and dolomite beds of the Famennian age. Intrusive rocks occur as a monzonite stock and syenite-aplite dykes of the Early Carboniferous age, granodiorite and plagiogranite-porphyry of the Upper Carboniferous complex as well as diabase and diabase-porphyry dykes. Upper Devonian rocks form the south-eastern limb of the Koksuisk anticline which is complicated by NS-trending faults, thrusts and steep faults of the predominant north-western trend. Mineralization is mainly confined to carbonate rocks and is localized in minor fissures, inter-layer zones of detachment and in hinges of dome-like folds and flexure bends.

Ore bodies occur as concordant sheets and lenses, and intersecting veins (Fig. 86). Arsenopyrite, pyrrhotite-bismuth and quartz-bismuth ores, are distinguished. Main ore minerals are arsenopyrite, pyrrhotite, pyrite, bismuthinite, native bismuth, cozalite and kobellite; gangue minerals include quartz, tremolite and chlorite; chalcopyrite, sphalerite, galena, bournonite, boulangerite, galenobismuthite, bismuth jemsonite as well as calcite, siderite, phlogopite and apatite are subordinate. The ore structures are massive, banded, mottled, disseminated, crustified and drusy; the textures are idiomorphic-granular, of replacement, corrosive and interstitial. Pre-ore contact-metasomatic alterations of rocks are expressed in tremolitization, actinolitization and K-feldspatization; wall-rock alterations consist of muscovitization, dolomitization, silicification and chloritization.

According to M. Sakharova, mineral formation developed in four stages: (1) quartz-tremolite; (2) quartz-bismuth; (3) arsenopyrite-bismuthinite; (4) post-ore chlorite-carbonate.
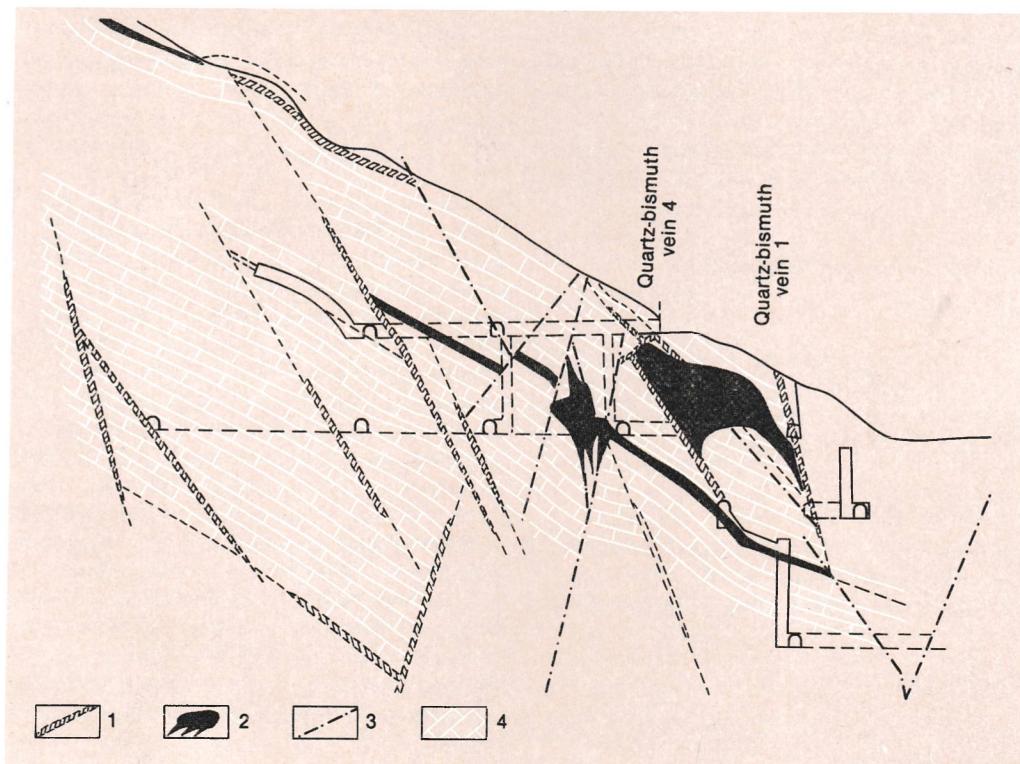
Fig. 86. The geological section of Ustarasai central part deposit. (After L. Miroshnikov):

1 – quartz-bismutite veins;   3 – faults;
2 – arsenic-bismutite replacement bodies;   4 – Famennian limestones

Deposits of
Penta-element Formation

Deposits of this formation are described in the chapter "Uranium Deposits".

VOLCANOGENIC HYDROTHERMAL DEPOSITS

Volcanogenic hydrothermal deposits are rare. In the USSR they are known in Central Asia (Adrasman). There are some deposits in other countries: in Bolivia (Tacna) and Italy (Bochegiano). The deposits are related to volcanogenic complexes of the dacite-liparite formation and are restricted to subvolcanic dikes, volcanic necks and plugs being localized in volcanic structures, synvolcanic faults and fissures which locally cut through the sedimentary-metamorphic basement. Ore bodies occur as branching veins, lenses and stockwork zones or, rarely, pipe-like bodies.

Mineral formation involved several stages: (1) quartz-arsenopyrite or, sometimes, pyrite-hematite; (2) chalcopyrite-bismuthinite; (3) galena-sphalerite; (4) post-ore carbonate. Host rocks are propylitized, silicified, sericitized, and chloritized, sometimes tourmalinized. Deposits were formed at a depth of 0.5-1 km. They belong to the chalcopyrite-bismuth and cassiterite-wolframite-bismuth ore formations.

Deposits of the
Chalcopyrite-bismuth Formation

ADRASMAN DEPOSIT is located in Central Asia. The area is composed of volcanogenic strata of the liparite composition. The deposit is confined to a quartz-porphyry neck and is controlled by intersecting sublatitudinal and sublongitudinal faults (Fig. 87). The major ore body has a pipe-like shape; it is traceable to a depth of more than 200 m from the surface. Other

ore bodies occur as lenses, veins and stockworks. The main ore minerals include pyrite, hematite, arsenopyrite, chalcopyrite, berrite and emplectite; quartz and chlorite are gangue minerals. Subordinate minerals are bismuthinite, native bismuth, arseno-pyrite, pyrrhotite, bornite and sphalerite as well as orthoclase and sericite. The ore structures are banded, crustified, drusy, veinlet, pocket and disseminated; textures are spherolite-radial, of solid solution decay, and emulsion. Hydrothermal alterations of host rocks are exhibited in chloritization, sericitization and silicification.

There are three stages of formation of ore mineralization: (1) pre-ore quartz-sericite; (2) pyrite-hematite; (3) a sulfide phase which produced bismuth minerals. The Adrasman deposit is dated as Late Permian-Early Triassic, and according to I. Kushnarev's data, it was emplaced in a vent zone of a volcano at a depth of 0.5-1 km.
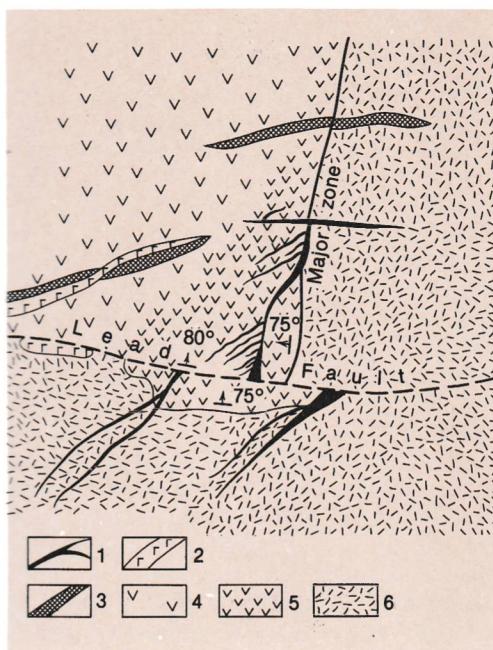
Fig. 87. Geological sketch map of the Adrasman copper-bismuth deposit. (After F. Volfson and A. Druzhinin):

1 – ore-bearing fissures;
2 – dikes of diabase porphyrite;
3 – dikes of quartz-syenite-porphyry;
4 – tuff-lavas of quartz porphyry cover;
5 – tuff-lavas of quartz porphyry forming a neck;
6 – Upper Paleozoic quartz porphyries

Deposits of Cassiterite-wolframite-bismuth Formation

Deposits of that ore formation are described in the chapter "Tin Deposits".

16 ANTIMONY DEPOSITS

Antimony belongs to a group of metals known in the ancient times when it was used for preparation of paints. The earliest description of its properties and methods of its extraction was given by the German alchemist V. Valentine in 1604. Commercial production of antimony started in the 20th century. Antimony gives strength, hardness and resistance against corrosion to alloys with lead, copper and zinc; it is characterized by fire-resistance of its compounds. The largest and traditional consumers of antimony are automobile, polygraphic, chemical and glass-making industries; it is also utilized in electrical and electronic industries, for production of paints and impregnating materials. Antimony is extracted from antimony, mercury-antimony and gold-antimony ores. As a by-product, it is recovered also from base metal, tin and tungsten ores. The cost of one ton of antimony is 3 950 US dollars. The production of the antimony concentrate in capitalist and developing countries in 1975 was 50 thous. tons; the total antimony reserves are estimated at one million 625 thous. tons. The unique deposits (Gravel Lot in SAR) comprise over 100 thous. tons of metal, large deposits – 100-30 thous. tons, average deposits – 30-10 thous. tons, and small deposits – less than 10 thous. tons. High-grade ores contain more than 5% antimony, ordinary ores – 5-2%, and low-grade ores – less than 2%.

GEOCHEMISTRY AND MINERALOGY

There are two stable antimony isotopes with the mass number of 121 and 123, the latter being somewhat more abundant. The crustal abundance of antimony (clarke) is $5 \cdot 10^{-5}\%$, its concentration coefficient being very high, of the order of 100 000. The value of abundance varies little for igneous rocks, being

somewhat increased up to $1 \cdot 10^{-4}\%$ in products of basaltoid magma. According to some geologist, the source of antimony, like that of mercury, is juvenile (subcrustal). Hydrothermal fluids containing antimony moved to upper layers of the earth crust through deep-seated faults. In the fluids antimony occurred in complex compounds in the form of thioantimonious acids of Na_3SbS_3 type. Antimony may be also transported in halides of the $SbCl_3$ type which possess high volatile ability. Antimony minerals were deposited at a temperature interval of 400-50 °C. Primary sulfide minerals containing antimony are oxidized under the exogenous conditions. Antimony sulfate thus formed is extremely unstable and is abruptly hydrolized passing into oxides and hydroxides (antimonous ochres). These are common in oxidation zone of endogenous deposits.

A total of 75 antimony minerals are known. The most important of them in primary ores is antimonite Sb_2S_3 (71.4%); less important in primary ores are: livingstonite $HgSb_4S_7$ (51.6%), berthierite $FeSb_2S_4$ (57.0%), gudmundite $FeSbS$ (57.8%), tetrahedrite $Cu_{12}Sb_4S_{13}$ (29.2%), jamesonite $Pb_4FeSb_6S_{14}$ (35.4%), boulangerite $Pb_5Sb_4S_{11}$ (25.7%), nadorite $PbSbO_2Cl$ (31%); in oxidized ores: valentinite Sb_2O_3 rhomb. (83.5%), senarmontite Sb_2O_3 cub. (83.5%), cervantite Sb_2O_4 (79.2%), kermesite Sb_2SO (75.0%) and stibioconite $(Ca, Sb)_2Sb_2O_6$ (O, OH) (76.4%).

METALLOGENY

Antimony deposits formed in relation to low-temperature hydrothermal fluids showing a remote paragenetic affinity with derivatives of the basaltic magma originated in subcrustal chambers. They were formed in the late stage of a geosynclinal cycle, and especially, during the tectono-magmatic reactivation of platforms and regions of completed folding. Because of this, antimony deposits frequently occur in the zones of deep-seated faults. No Caledonian or more ancient antimony deposits have been so far discovered. Some of them were emplaced in the Hercynian metallogenic epoch, but the major bulk of these deposits were formed in the Kimmerian, and especially, Alpine epochs.

Most of the antimony deposits, except the South African ones, are located within three global ore belts, namely, Mediterranean, Central Asian and Pacific.

TYPES OF COMMERCIAL DEPOSITS

These include: (1) plutonogenic hydrothermal; (2) volcanogenic hydrothermal; (3) stratiform.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

These are represented by two ore formations: quartz-antimonite mono-metal antimony (occasionally with gold) ores and complex ores containing Sb, As, Au, Aq, W, Cu, Pb, and Zn.

Deposits of Quartz-antimonite Formation

These types of deposits are known in the USSR in Yakutia (Sarylakh) and in the Krasnoyarsk region (Razdolninskii, Udereiskii); outside the USSR they are known in Czechoslovakia (Pezinok), SAR (Gravel Lot), Turkey (Ezdemir), Thailand (Rajatburi), Australia (Blue Speck), Bolivia (Chilcobiya) and in Mexico (Texocates). The deposits occur in rocks of the aluminosilicate composition – sandstones, shales, schists and gneisses. They are confined to regional faults, crush zones and fissure zones. The shape of the ore bodies is essentially vein-type. Systems of en echelon veins are traceable for many kilometres along the strike and for 1 000-1 200 m along the dip without a marked change of their mineral composition. Individual ore veins show the strike-wise and dip-wise length of up to 300-500 m; their width varies from 0.1 to 5-6 m, attaining in swells 20 m, the average thickness being 1-2 m. The antimony content in high-grade ores varies from 2-3 to 40%, the average being 10%.

The mineral composition of the deposits is rather simple. The main ore mineral is antimonite; gangue mineral – quartz; berthierite, gudmundite, pyrite, arsenopyrite,
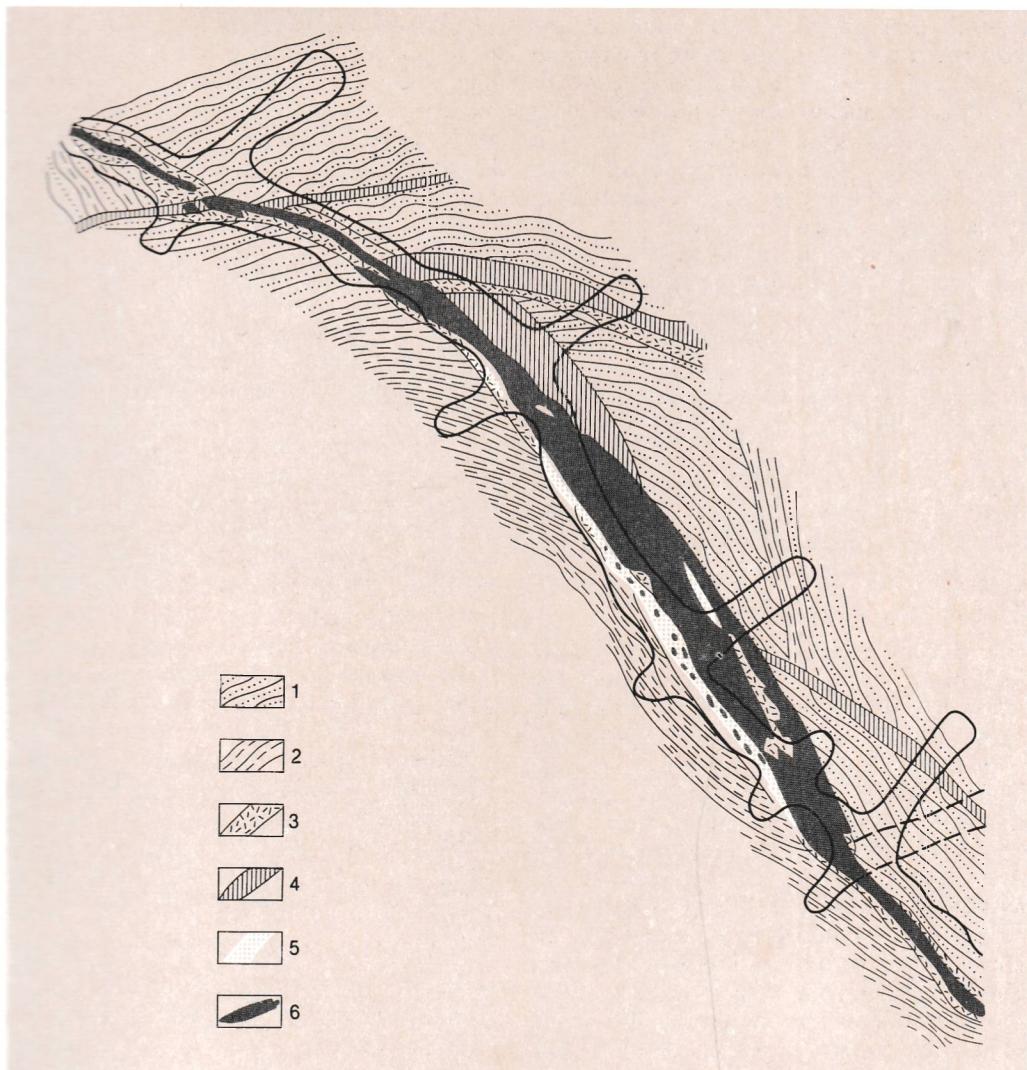
Fig. 88. Structure of the body from the Sarylakh deposit. (After P. Polyansky):

1 – sandstones;
2 – aleurolites;
3 – pyroclastic rocks;
4 – zones of crush and foliation;

5 – quartz vein with pocket-disseminated antimony ore;
6 – massive antimony ore

chlorite, sericite and siderite are subordinate. Ore deposition occurs in two main stages: the early quartz stage, and the late sulfide stage. Hydrothermal alterations of host rocks consist of silicification, chloritization and pyritization accompanying the early stage of ore deposition.

SARYLAKH DEPOSIT is located in Yakutia. The ore-enclosing rocks consist of steeply dipping beds of sandstones and aleurolites of the Upper Triassic age. Igneous rocks occurring as a stock of quartz diorite-porphyries belong to the Late Jurassic complex of minor intrusions. The deposit is controlled by the NW-strike of deep-seated fault that separates areas of tense linear folding from those of weak dislocations.

The ore body is represented by a quartz-antimonite vein restricted to the

central part of the crush zone of the northwestern trend whose width amounts to 15-18 m (Fig. 88). The ore vein extends for hundreds of metres along the strike and along the dip being from 0.1 up to 3.3 m wide in swells which occur in the sandstone beds. The main ore mineral is antimonite; gangue mineral – quartz, pyrite and arsenopyrite are subordinate. Massive ore structures are typical of the hanging wall of the vein, while in the footwall and at the pinching out portions of the vein the nodular, veinlet and disseminated types of ores are common. At the near-surface parts of the vein antimonite appears to be partly oxidized and replaced by senarmontite and valentinite. Near-ore alterations of host rocks are expressed in silicification, sericitization and in pyritization.

Deposits of
Complex Ore Formations

Plutonogenic hydrothermal deposits of these formations comprise deposits with the following ores: scheelite-gold-antimonite (Vosi, China), wolframite-antimonite-cinnabar (Barun-Shiveya, Transbaikal region; Siang, China), antimonite-argentite-galena-sphalerite (Sunshine, the USA) and cassiterite-antimonite (Sary-Bulak, Central Asia). These deposits are normally of the average and small size. The host rocks are represented by terrigenous sediments, in places by carbonate and granitoid rocks. Faults, fissures and, less frequently, folds serve as ore-enclosing structures. The shape of the ore bodies is usually vein-like, but stockwork, pipe-like and lenticular concordant configurations are also observed. Ore bodies are traceable along the strike for tens-first hundreds of metres, along the dip – for 250-300 m, their average width varying from 0.1 to 2-3 m.

The mineral composition is rather complex. The main ore mineral is antimonite; berthierite, gudmundite, arsenopyrite, pyrite, ferberite, scheelite, chalcopyrite, galenite, sphalerite, native antimony, jamesonite, and boulangerite are subordinate; the main gangue mineral is quartz, occasionally carbonates. Ore deposition occurred at an interval of 300-200 °C in two major stages: early berthierite-antimonite and late

scheelite-ferberite-antimonite stages. A vertical zonality is very distinct: complex ores containing chalcedony-like quartz, ferberite, scheelite, cinnabar and antimonite are localized in the middle and upper horizons passing with depth into simpler quartz-antimonite ores.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

These are known in Romania (Baia-Mare, Baia-Sprie), Turkey (Tekger, Akdashanaya Dere), Algeria (Hamman N'Bail, Hammimat) and in the USA (Yellow Pine). They are localized in the regions of young and present-day volcanism and in areas where thermal springs are abundant. The deposits are related to andesite and rhyolite complexes. They are frequently confined to the rocks of vent and subvolcanic facies, but are also known to occur in the calcareous-clayey deposits. Necks, rings and radial fissures, as well as tectonic zones of crush and jointing serve as ore-enclosing structures. The ores are represented by branching veins, stockworks, pipe-like, concordant lenticular and complex mushroom-shaped bodies. The size of the bodies is small, a few tens of metres in length along the strike, up to 200-250 m along the dip, their thickness varying from 0.1 to 10 m.

There are two types of ores, the specific antimony and complex ores represented by arsenic-antimony, antimony-silver and antimony-tin deposits. The main ore mineral is antimonite, occasionally oxichlorides of antimony and lead (nadorite) or simple oxides, like servantite; livingstonite, grey ores, galenite and sphalerite are subordinate; gangue minerals consist of chalcedony quartz, sericite and carbonate. In the oxidation zone common are servantite, stibiconite, limonite. Hydrothermal alterations of the host rocks consisted in silicification and kaolinization. Ore deposition took place during a short-time stage.

STRATIFORM DEPOSITS

These are known in the USSR in the Central Asia (Kadamdzhai, Dzhidzhikrut,
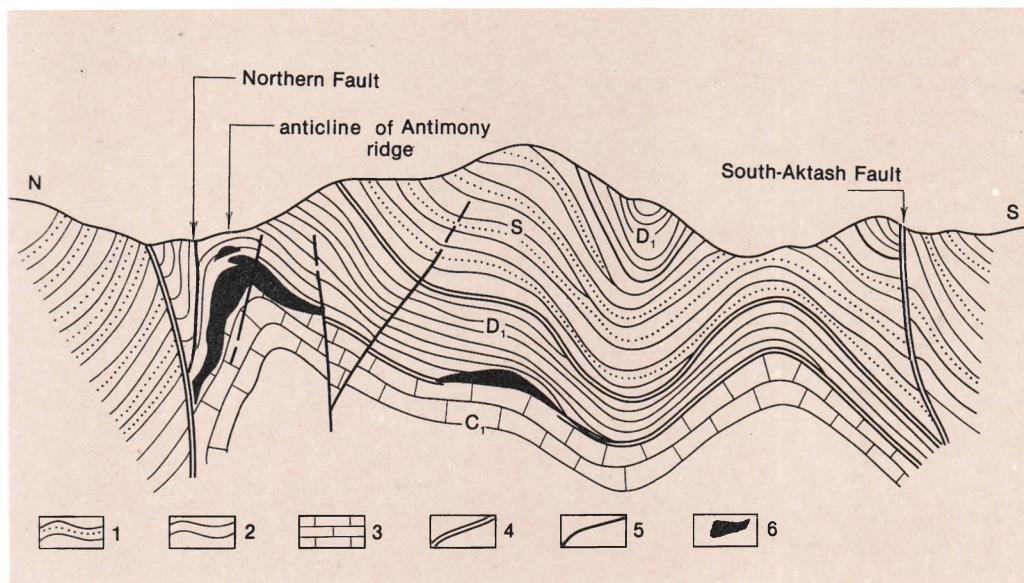
Fig. 89. Geological section of the Kadamdzhai deposit. (After N. Nikiforov):

1 – Silurian sandy shales;
2 – Lower Devonian shales interbedded with sandstone and gravelstone;
3 – massive limestones of Lower Carboniferous;
4 – thrusts;
5 – faults;
6 – hornfel-jasperoid breccias containing ore

Terek), also in China (Sin Khuan Shan), Bulgaria (Rybnovo), Italy (Peretta), and in Mexico (San-Jose). These deposits were formed in miogeosynclinal zones and on platforms being confined to carbonate beds overlain by shales. Typical are gently folded structures, brachyanticlinal and box-like folds. Folding appears to be often complicated by thrusts and steep faults serving as ore-feeding channels. In gently dipping parts of the folds frequently in their hinge parts there occur thick (up to 200 m) interformational beds of silicified limestones – jasperoids, commonly brecciated. Ore bodies of sheet-like or lenticular shape are mainly confined to the upper part of the succession under the shale screens. The ore bodies extend for many hundreds of metres to first kilometres along the strike and up to 1 000 m along the dip, having the thickness up to 40-50 m. Stratiform deposits belong to the quartz-fluorite-antimonite formation. The ores are of the antimony and antimony-mercury type. The antimony content in them is 1-12%, on the average 1.5-3%.

The main minerals are antimonite and quartz; cinnabar, markasite, pyrite, arsenopyrite, boulangerite, jamesonite, sphalerite, chalcopyrite, orpiment and realgar, as well as calcite, fluorite, sericite and barite are subordinate. Hydrothermal alterations of the host rocks are attributed to the pre-ore stage and manifest themselves in silicification, carbonatization and pyritization. Ore deposition occurred in 2-3 stages. At the early stage running at the temperature of 205-105 °C the main bulk of antimonite and cementation quartz was deposited. During the later stage at a temperature interval of 100-70 °C barite and calcite were crystallized accompanied by deposition of realgar, orpiment and a small quantity of antimonite.

KADAMDZHAI DEPOSIT is located in the Central Asia. The area of the deposit is composed of massive and thick-bedded carbonate rocks of Lower Carboniferous and shales of Middle Carboniferous. These are overlain by Devonian and Silurian terrigenous sediments. Dikes of Late Hercynian diabase porphyries are occasionally observed. The deposit is restricted to the western closure of the Aktash sublatitudinal

anticline whose core is composed of Lower Carboniferous limestones and the limbs – of Middle Carboniferous shales. Hinge parts of small box-like brachyanticlines that complicate the pericline of the Aktash fold contain interformational sheet-like bodies of ore-bearing breccias, hornfels and jasperoids. The ore-bearing breccias are also found along the faults that complicate the folding. The interformational breccias attain their maximum thickness (up to 25-30 m) in the hinge parts of the anticlines; it decreases at their limbs (Fig. 89). The breccias consist of angular fragments (0.2-2 cm) of silicified limestones and shales cemented by quartz and antimonite. Distribution of ore in the breccias is irregular; rich concordant antimonite bodies are localized under the shale screen and tend to occur in anticlines with a small radius of flexure which is complicated by faults. Common are lenticular and vein-like ore bodies occurring at the intersection of fissures.

The main ore mineral is antimonite; pyrite, markasite, realgar, orpiment, chalcopyrite, sphalerite and galena are subordinate; the main gangue mineral is quartz; subordinate gangue minerals consist of fluorite, calcite, barite, dickite and sericite. The oxidation zone contains abundant kermesite, velentinite, senarmontite, hydroservantite, stibiconite and aragonite. The ores are characterized by massive, brecciated, disseminated and banded structures; less frequent are stringer, pectinate, cockade and drusy structures; textures are coarse-crystalline, radially fibrous, fine-grained and metacolloidal.

Hypogenous emplacement of the ores occurred in three stages. Metasomatic silicification which resulted in formation of hornfels after shales and of jasperoids after limestones took place during the first stage; this process was accompanied by insignificant sericitization and by the development of sparse impregnation of pyrite, chalcopyrite, galenite and sphalerite. During the second stage the breccias of the silicified rocks were cemented by quartz, antimonite, calcite and by fluorite. The third stage resulted in formation of veinlets of the calcite-realgar-orpiment composition. The ores of the Kadamdzhaï deposit were

formed, judging from the brecciated structures and metacolloidal textures, at shallow and moderate depths.

17 MERCURY DEPOSITS

Native mercury was known as far back as over 2 000 years B. C. Cinnabar was used by ancient Greeks and Romans as paint, medicinal and cosmetic materials. In the 9-11th centuries mercury was mined in Southern Europe and in Central Asia. Its application is based on the fact that mercury is volatile under the normal temperature, expands intensely when heated and is capable to dissolve other metals producing amalgams with Au, Aq, Zn, Pb, and Al. Mercury is utilized in medicine, chemical, electrical and instrument-making industries, in explosives, energetics, thermonuclear technology and in agriculture. It is rather toxic and should be treated very carefully. Mercury is extracted from mercury, mercury-antimony, mercury-arsenic and mercury-gold ores. As a by-product it is also recovered from base metal, tungsten and tin ores. The price of one ton of mercury in 1975 was 6 400 US dollars. Mercury production in the capitalist and developing countries in 1975 to 5 300 tons.

Unique deposits (Almadén in Spain) comprise over 1 000 thous. tons of metal, very large deposits have 100-25 thous. tons, large ones – 25-10 thous. tons, average deposits – 10-3 thous. tons, and small ones – less than 3 thous. tons. High-grade ores contain over 1% mercury, ordinary ores – 1-0.2%, and low-grade ores show less than 0.2% mercury.

GEOCHEMISTRY AND MINERALOGY

A total of 7 stable mercury isotopes are known with the mass numbers of 196, 198-202 and 204, among which ^{202}Hg is predominant. The crustal abundance (clarke) of mercury is $8.3 \cdot 10^{-6}\%$, its concentration coefficient is extremely high attaining some 100 000. The mercury content in igneous rocks of various composition approaches the clarke values being increased up to
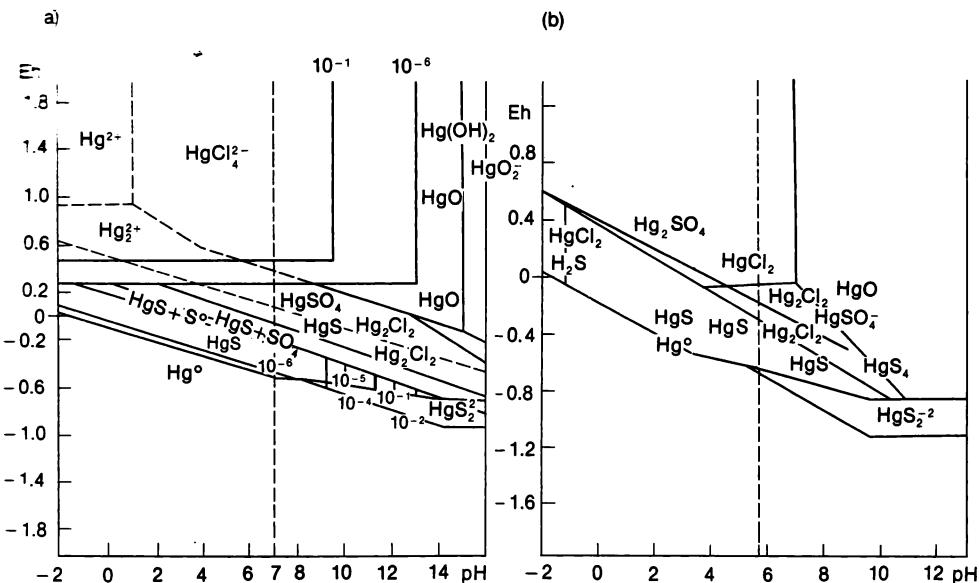
Fig. 90. Stability relationships between certain mercury compounds in water at 25 °C (a) and at 250 °C (b). The total of dissolved sulphur $1 \times 10^{-1}\%$, chlorine $1 \times 10^{-1}\%$. Stability fields of sulfide and chloride complexes are plotted for the activity of components being 1×10^{-1} and 1×10^{-6}. (After A. Obolenskii).

$1 \cdot 10^{-4}$-$1 \cdot 10^{-2}\%$ in alkaline rocks, differentiates of the basaltoid magmas. According to many scientists, the source of mercury is juvenile (subcrustal). Hydrothermal fluids containing Hg, Sb and As were transported from the mantle through deep-seated faults to the upper layers. The fluids were highly concentrated, alkaline, of the sulfur-chloride-carbonate composition.

Mercury in these fluids was transported in the form of sulfide complexes (HgS_2^{2-}) which are stable in alkaline solutions under the low oxidizing potential Eh (Fig. 90). Deposition of sulfides from solutions of these complexes is caused by oxidation and by a decrease in the pH value of the solutions. The role of acid solutions and chloride complexes ($HgCl_4^{2-}$), which are stable at the low values of pH and under high positive values of Eh, is limited by oxidation zones of mercury deposits, as well as by fields of solfatara and fumarole activity. In the case of acting volcanoes and thermal springs, mercury may migrate in a gaseous state and in a gaseous phase of hydrotherms.

Mineral formation in the mercury deposits occurs at a temperature interval of 350-50 °C and pressures from 1500 to 300-400 kgf/cm². Under the near-surface conditions the pressure may drop to 1 kgf/cm². The principal natural factors causing deposition of the ore are: (1) interaction of the fluids with host rocks; (2) oxidation under near-surface conditions by atmospheric oxygen; (3) dilution by vadose waters; these factors operate along with a general decrease of temperature and pressure.

The main ore mineral is mercury sulfide (cinnabar) which is stable in the oxidation zone, and is preserved at the exposures of the mercury ore bodies being only slightly transformed into secondary powdery cinnabar, native mercury and calomel.

A total of 20 mercury minerals are known, but only cinnabar trig. HgS (86.2%), metacinnabar cu. HgS (86.2%), native mercury Hg, grey ore – schwatzite (Hg, Cu)$_{12}$·Sb$_4$S$_{13}$ (17%), livingstonite HgSb$_4$S$_7$ (22%), cordeorite Hg$_3$S$_2$Cl$_2$ (82%) and calomel Hg$_2$Cl$_2$ (85%).

METALLOGENY

Mercury deposits are postmagmatic hydro-thermal low-temperature types of deposits. They exhibit a remote paragenetic link with differentiates of deep-seated subcrustal chambers of basaltoid magmatism. They were mainly emplaced during the late stage of the geosynclinal cycle and also in relation to tectonomagmatic reactivation of platforms and regions of complete folding. These deposits are frequently restricted to deep-seated fault zones; they also occur within the volcanic belts.

No Caledonian or more ancient mercury deposits have been so far discovered. Apparently, such deposits were destroyed either by erosion or by metamorphic processes. The Hercynian metallogenic epoch was very essential. However, the main bulk of mercury deposits was emplaced during the Kimmerian and Alpine epochs. Mercury ore-bearing provinces are located within three global mercury belts, namely, Mediterranean, Central-Asian and Pacific.

TYPES OF COMMERCIAL DEPOSITS

The following commercial types of mercury deposits are distinguished: (1) plutonogenic hydrothermal; (2) volcanogenic hydro-thermal; (3) stratiform.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

These are known in the USSR in Transbaikal region (Barun-Shiveya, Ildikan), Central Asia (Tepar) and in Mountainous Altai (Chagan-Uzun); abroad they are found in China (Vosi), Ireland (Gortdram), Turkey (Gyumyusler), Tunisia (Jabel-Andja) and in the USA (New Almadén, New Indria). The deposits occur in terrigenous, carbonate, granite, ultrabasic and metamorphic rocks and are confined to regional faults, occasionally deep-seated ones, and to fissure zones. Ore bodies have a vein, pipe, lense, stockwork and pocket shape. Most frequent are branching veins of the small size – first hundreds of metres along the strike and along the dip, their width being 1-2 m. The

pipe-like bodies with a cross-section being up to tens of square metres are traceable to a depth of 1 000 m and even deeper.

Plutonogenic hydrothermal deposits are represented by two main ore formations: (1) quartz-chlorite-sericite-cinnabar (Barun-Shi-veya and Ildikan in Transbaikalia, Tepar in the Central Asia, Vosi in China, Gortdram in Ireland, Gyumyusler in Turkey and Jabel-Adja in Tunisia); (2) magnesium-carbonate-cinnabar (listvenite) (Chagan-Uzun in the Mountaneous Altai, New Almadén and New Indria in the USA).

Deposits of Quartz-chlorite-sericite-cinnabar Formation

Deposits of this formation are characterized by a comparatively small size and by the presence of complex ores, namely, mercury-antimony, mercury-gold-silver, mercury-tungsten-arsenic, mercury-tin, mercury-copper and mercury-base metal. The main ore minerals are cinnabar and schwatzite; antimonite, ferberite, scheelite, arsenopyrite, galena, sphalerite, chalcopyrite are subordinate; the main gangue mineral is quartz; carbonates, sericite, chlorite, fluorite and barite are subordinate gangue minerals. Hydrothermal alterations of the silicate rocks consisted in silicification and in chloritization, and those of carbonate varieties – in silicification, carbonatization, baritization and in fluoritization.

Ore deposition, according to V. Fe-dorchuk, occurred in several stages at a temperature interval of 250-150°C from concentrated (up to 10-100 ppm) mul-ticomponent hydrothermal solutions. A vertical zonality is distinct (though of a small span) and manifests itself in accu-mulation of mercury minerals, which are the last to precipitate, within the upper horizons of the deposit. Spatially and probably paragenetically, these deposits are associated with intrusives of the acid composition.

Deposits of Magnesium-carbonate-cinnabar Formation

These are characterized by the presence of comparatively simple mercury ores. The predominant ore mineral is cinnabar, subor-dinate minerals are pyrite, arsenopyrite and antimonite; typical are rare minerals, like

siegenite, bravoite, millerite and gersdorffite. The main gangue minerals are ferruginous dolomite, dolomite, ankerite and quartz; magnesite, calcite, dickite, bitumens are subordinate gangue minerals; relict minerals consist of talc, serpentine, fuchsite and chromite.

According to V. Kuznetsov, the process of ore deposition involves three main stages: early magnesium-carbonate-quartz with pyrite, arsenopyrite, antimonite and cinnabar, the main productive, dolomite-cinnabar stage (150-100 °C), and post-ore calcite stage. The pre-ore metasomatites are represented by listvenite consisting of quartz and carbonates (magnesite, breunnerite and dolomite). Wall-rock alterations are manifested in argillization, silicification, carbonatization and in additional listvenitization. In spite of a considerable vertical scale of mineralization reaching in some of the deposits 1 000 m and more, no marked variation in the ore material composition is observed. Deposits of the magnesium-carbonate-cinnabar type are generally typical in deep-seated fault zones accompanied by ultrabasic (serpentinite) belts with which these deposits appear to be spatially and structurally associated.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

These are known in the USSR in Chukotka (Plamennyi), Kamchatka (Chempura, Anapel), Amur region (Lanskoi), Central Asia (Aksagata), Transcarpathian Area (Bolshoi Shayan, Borkut); also abroad in Italy (Monte-Amiata), Jugoslavia (Idria), Algeria (Islaim), Turkey (Kazyzmakh), Japan (Itomuka) and in the USA (Mac-Dermit, Opalite, Cordero, Sulphur Bank). They are usually located in the regions of the present-day or young volcanism and in the areas where thermal springs are abundant. These deposits are associated with andesite, trachyrhyolite and rhyolite formations which are differentiates of basalt magmas. They are confined to lavas, tuffs, extrusive tuffites, subvolcanic and vent facies, and to terrigenous-carbonate formations associated with volcanic rocks. The deposits are often controlled by volcanic structures, like calderas, volcano-tectonic depressions, volcanic domes, subvolcanic bodies and necks, synvolcanic ring fractures, faults and thrusts, as well as by zones of jointing.

Ore bodies occur as veins, stockworks, pipes, pockets, lenses, sheets or more complex bodies. They usually dip steeply, but the sheet-like bodies and upper portions of the mushroom-shaped bodies are flat-lying and concordant with the enclosing volcano-sedimentary deposits of caldera lakes. Dimensions of the ore bodies are commonly small—a few hundreds of metres along the strike and 200-250 m along the dip, their thickness varying from several metres to a few tens of metres, except large deposits (for example, Monte-Amiata in Italy) which are traceable to a depth of about one km.

The ores are characterized by the complex mineral composition. Apart from cinnabar, the mercury minerals include usually metacinnabar and native mercury, in places calomel and corderoite are observed. Realgar, orpiment, antimonite, markasite, pyrite, galena, sphalerite, chalcopyrite, argentite, pyrargyrite, argentiferous gold and silver are present in small amounts. Among gangue minerals typical are opal, native sulphur, alunite, kaolinite, montmorillonite, gypsum, barite; less abundant are carbonates, halloysite, zeolite and solid hydrocarbons. The mercury content varies from 5-3% in high-grade ores to 0.2-0.1% in low-grade ores. Mercury ores are commonly emplaced in a single stage, however, sometimes at the earlier stage deposition of galena, sphalerite and chalcopyrite takes place.

Volcanogenic hydrothermal deposits belong to the opalite-cinnabar formation which is associated with other volcanogenic deposits of sulphur, arsenic, antimony or gold-silver ones. This formation consists of 5 mineral types: carbonate-polyargyrite-cinnabar (Monte-Amiata, Idria in Yugoslavia), quartz-dikkite-cinnabar (Cordero in the USA), opalite-cinnabar (Opalite, McDermit in the USA), schwatzite (Kulpolnei in Chukotka; Rudnjana in Czechoslovakia; Los Mantos in Chile; Ord in the USA), travertine (Anapel in
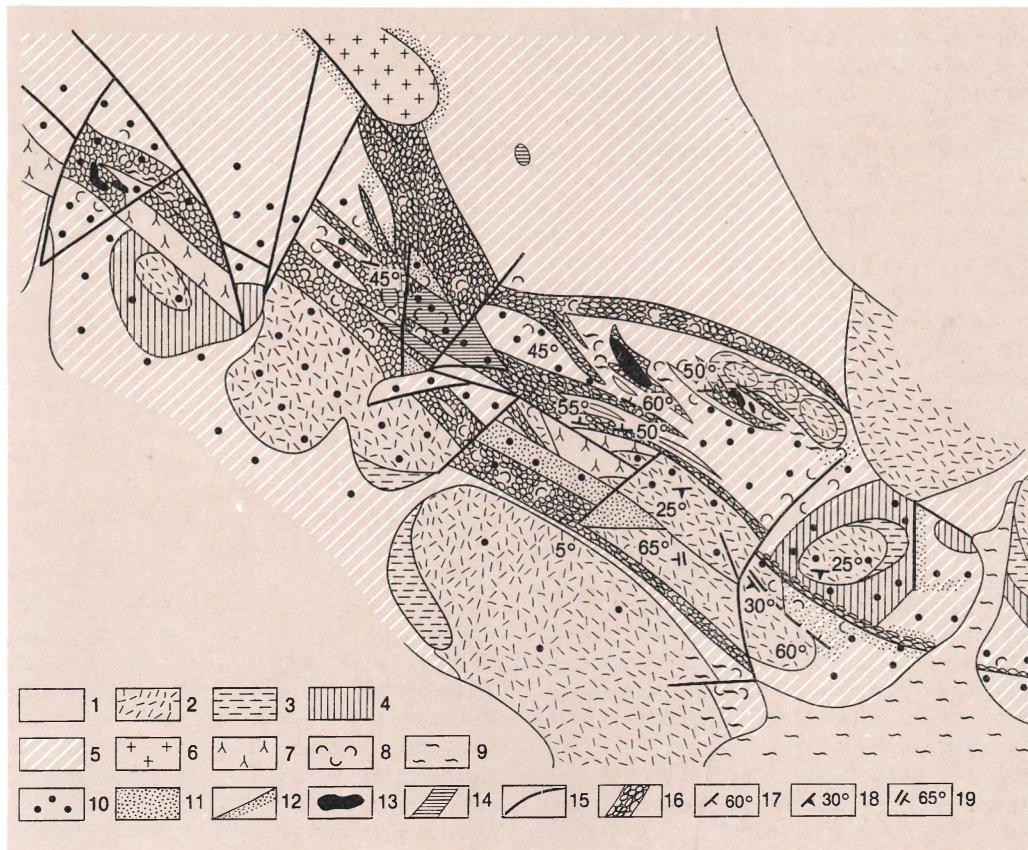
Fig. 91. Geological sketch map of the Plamennyi deposit. (After P. Babkin)

1 – Quaternary sediments;
2 – fine porphyric liparites;
3 – liparites showing a flow structure;
4 – tuff-lavas and tuffs of liparite composition;
5 – coarse porphyric liparites;
6 – diorites;
7 – andesites;
8-11 – altered rocks: 8 – kaolinized,
   9 – chloritized,
  10 – pyritized,

11 – silicified,
12 – zones of contact metamorphism;
13 – ore bodies;
14 – manifestations of antimony ore;
15 – faults;
16 – crush zones;
17-19 – dip and strike of:
  17 – contacts of beds and crush zones,
  18 – flow structures in liparites,
  19 – joint structures

Kamchatka; Sulphur Bank in the USA). These mineral types occasionally form a vertical zonality within the ore fields, like for example, in the Opalite ore field in the USA. There hydrothermal fluids rising along the zone of the major ore-controlling fault formed, at a depth interval from 75 to 250 m, a column-like body of rich quartz-dickite-cinnabar ores (Cordero deposit); moving further upwards at 0.75 metre depth, stockwork ores in crushed opalites (Opalite deposit) were deposited under near-surface conditions and finally on the surface, in lacustrine sediments a body of volcanogenic-sedimentary ores was formed, that contains, apart from cinnabar, metacinnabar and native mercury, also oxichloride compounds of mercury – corderoite and mackdermitite (McDermit).

Thus, mercury volcanogenic deposits are characterized by near-surface (tens-first hundreds of metres) and even, sometimes, by surface conditions of the ore formation. The deposits were formed in a zone of circulation of vadose waters enriched in oxygen. Mixing of these waters with deep-originated hydrothermal solutions caused such non-stable minerals like metacinnabar

and native mercury to precipitate. The ore was deposited from weak alkaline, occasionally weak acid gaseous-liquid solutions of the chloride-sodium composition. According to thermometric studies, the temperature range of ore deposition is rather wide – from 400 to 70 °C. However, the actual ore deposition took place mainly at a temperature interval of 190-70 °C (Plamennyi and Chempura deposits). In cases of thermal springs mercury ores were deposited at a temperature lower than 100 °C.

PLAMENNYI DEPOSIT is located in Chukotka, at the margin of the Okhotsk-Chukotka belt. The area is composed of Lower Cretaceous lavals, tuff breccia, ignimbrites and liparite tuffs forming a volcanic dome. These rocks are intruded by stocks of subvolcanic andesites, granitoids and diorites of the Cretaceous age. The volcanic strata lying almost horizontally is complicated by a series of steeply dipping faults which are accompanied by breccias and by zones of metasomatites (Fig. 91).

The main ore body having a sheet-like shape occurs conformably in the upper part of the liparite cover whose age is 102-105 m.y. (Aptian-Albian); there are also lenticular ore bodies confined to the transverse fault zones. Mercury, antimony-mercury and antimony ores are distinguished. The main ore minerals are cinnabar and antimonite, while quartz is the main gangue mineral; pyrite, markasite and realgar and also chalcedony, kaolinite, sericite, hydromicas, adular and chlorite are subordinate minerals. The ores are characterized by massive, disseminated, veinlet-type, mottled, crustified and drusy structures, and by allotriomorphic, corrosion, cementation textures and by a texture of filling.

Hydrothermal metasomatites were formed in the pre-ore stage. These show a zonal distribution: the central zone, 3-5 m thick, is composed of monoquartzite quartz-kaolinite metasomatites, the intermediate zone consists of quartz-sericite metasomatites with mercury mineralization, and the outer zone is represented by weakly altered (silicified) liparites. Ore deposition occurred
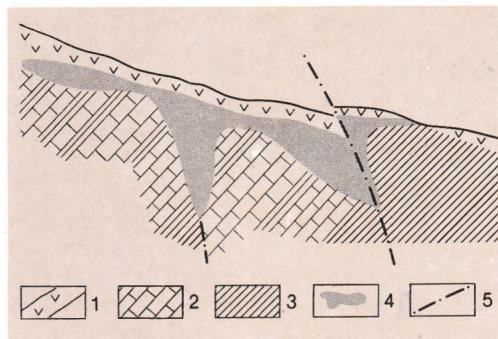
Fig. 92. Geological sketch map of the Monte-Amiata deposit:
  1 – Quaternary trachyte flow;
2-3 – Cretaceous rocks:
  2 – limestones;
  3 – shales;
  4 – ore body (mineralized breccia);
  5 – faults

in a single stage. Minerals of two paragenetic associations, early quartz-antimonite and late quartz-cinnabar, were deposited at a temperature of 145-70 °C.

A horizontal zonality of the mineralization manifests itself in a substitution of antimony ores localized in the central portion of the deposit for mercury-antimony and then mercury ores occurring at its flanks. The age of the deposit is Late Cretaceous. It is associated with acid differentiates of the volcano-plutonic complex.

MONTE-AMIATA DEPOSIT is situated in Italy. A total of 100 thous. tons of mercury have been recovered for the last 100 years; the total reserves of the remaining ores are estimated at 240-350 thous. tons. The area of the deposit is composed of Upper Cretaceous limestones and shales which are overlain by hypersthene-labradorite trachytes of the Quaternary Monte-Amiata volcano. The deposit is confined to the NE-striking shear fault.

The ore-bearing sequence consists of interformational tectonic breccia which is localized in a gently dipping contact zone between the sedimentary rocks and volcanics (Fig. 92). The thick breccia is traceable for 30 km in length and for 10 km in width. It has a blanket-like shape and consists of mineralized blocks of crushed shales and limestones cemented by clayey

material. The ore-bearing zone comprises ore bodies in the form of lenses (5-10 m wide), pockets and pipes; these bodies extend to a depth of 100-150 m, their thickness decreasing with depth. The mercury content at the upper horizons is 3-4%, at lower layers it drops to 0.7% and even lower; the average mercury content calculated for the entire deposit is 1.5-1.8%. The main ore mineral is cinnabar; realgar, orpiment, native sulphur and fluorite are subordinate. The ores are characterized by massive, brecciated, veinlet-type and disseminated structures and by fine-grained and collomorphic textures. The host rocks are subjected to intensive hydrothermal alteration (argillization).

The age of the deposit is Alpine; it is associated with volcanism being confined to thermal springs and gaseous emanations of the carbon dioxide-hydrosulfide composition in fault zones.

STRATIFORM DEPOSITS

These are known in the USSR in Donbass (Nikitovka), Central Asia (Khaidarkan, Chauvai), Caucasus (Sakhalinsk) and in Yakutia (Levosakyndzhin); abroad these deposits are found in Spain (Almadén), China (Van Shan), Peru (Juankavelika). Stratiform deposits are situated in regions of stabilization of geosynclines or in zones of platform reactivation. They are characterized by the absence of direct links with igneous rocks, and therefore belong to amagmatogenic or telethermal deposits. These deposits occur in terrigenous or carbonate rock complexes which are deformed into dome-like and box-like anticlines, occasionally dislocated in a complex way. Folding is complicated by thrusts and transverse faults.

Ores occur mainly as conformable sheet and lenticular bodies lying in porous sandstones or brecciated silicified limestones. The conformable bodies appear to be associated with cross-cutting veins and stockworks. The thickness of the ore-bearing horizons varies from a few metres to 30-40 metres; they are traceable for many hundreds of metres-first kilometres along the strike, and for 800-1 000 m along the dip.

Though the type of ores remains the same in both directions, the thickness of ore bodies and the mercury content decrease to the depth, amounting to 10-15% in the upper horizons and decreasing to less than 1% at the deep ones. Multi-stage ore bodies are also observed.

The main ore mineral is cinnabar, occasionally antimonite; metacinnabar, realgar, orpiment, pyrite, markasite, arsenopyrite, livingstonite, galena, sphalerite, chalcopyrite and grey ores are subordinate; main gangue minerals are quartz, calcite, dickite and fluorite; less common are dolomite, barite, chalcedony, sericite, montmorillonite and nacrite.

The process of ore deposition was continuous. During the pre-ore stage hydrothermal alteration of the host rocks occurred, involving silicification, that resulted in formation of jasperoids (220-140 °C and under pressure of 330 ± 10 kgf/cm^2), dickitization, carbonization and argillization. Ore deposition developed in 3-5 stages: during the initial stages having a temperature interval of 170-120 °C antimonite was crystallized, being substituted for cinnabar during the subsequent stages, when the temperature dropped down to 135-120 °C. The post-ore stage (240-105 °C) was marked with formation of quartz-fluorite-calcite veinlets. According to V. Fedorchuk, the hydrothermal solutions were of a low concentration (up to 5 g/l) and included only a few components. The depth of the deposition of stratiform mercury deposits is about 1 000 m, but the vertical span of the mineralization in some cases appears to be over 2 000 m.

The following three ore formations among stratiform deposits can be identified: (1) quartz-dickite-cinnabar (Nikitovka in Donbas; Almadén in Spain); (2) quartz-fluorite-antimonite-cinnabar (Khaidarkan in the Central Asia); (3) carbonate-cinnabar (Adyrkou in the Central Asia, Lavosakyndzhin in Yakutia; Van Shan in China).

Deposits of
Quartz-dickite-cinnabar Formation

NIKITOVKA DEPOSIT is located in Donbas. The area is composed of the Middle Carboniferous sequence consisting of
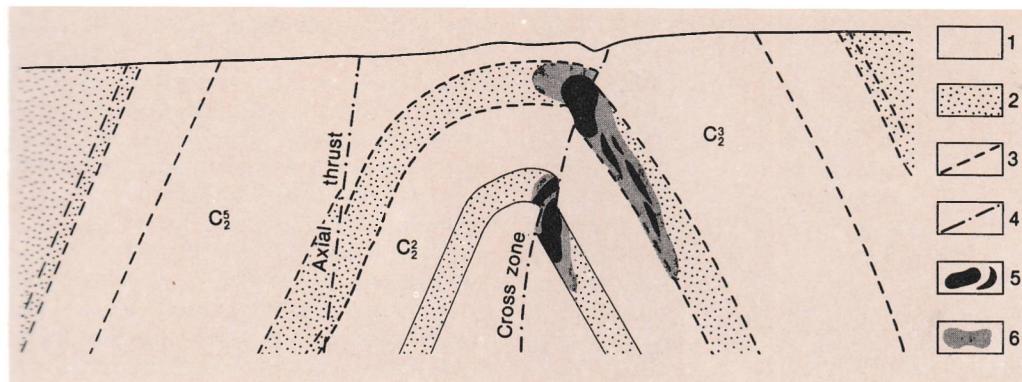
Fig. 93. Geological section of the Nikitovka deposit. (After S. Kirikilitse):

1 – shales;
2 – sandstones;
3 – coals;

4 – faults;
5 – ore bodies;
6 – mineralized rocks

interbedded sandstones, shales, limestones and coals. The deposit is confined to domes that complicate the anticline of the sublatitudinal strike. Folding is accompanied by thrusts, including the Nikitovka Thrust ("Cross-cutting" zone). These thrust faults are associated with diagonal faults and jointing, which is cross-cutting or conformable to bedding.

Ores occur as conformable sheet bodies and veins, the former being restricted to the contact zone between the Nikitovka thrust fault and ore-enclosing sandstones, and to fissured apical parts of the domes (Fig. 93). The vein bodies occur in transverse and in diagonal fractures. The ores are monometallic (mercury). The main ore mineral is cinnabar; antimonite, arsenopyrite, pyrite and markasite are subordinate; gangue minerals consist of quartz, dickite, sericite and ferruginous carbonates. The ores are characterized by disseminated and veinlet-like, less frequently massive and brecciated structures and by metacolloidal, cementation textures; textures of filling and mutual boundaries are also observed.

Ore deposition involved 5 stages: (1) arsenopyrite; (2) quartz-arsenopyrite; (3) antimonite-carbonate; (4) antimonite-cinnabar; (5) dickite-antimonite-cinnabar. The temperature of quartz deposition is 290-240 °C, and that of cinnabar and antimonite is 150-120 °C. Hydrothermal alteration of the host rocks manifests itself in silicification, argillization, dickitization

and carbonization. The age of the deposit is Late Hercynian or Kimmerian. The isotopic composition of sulphur of the sulfides is monotonous and similar to that of meteorite sulphur. Evidently, the ore-containing solutions were related to subcrustal chambers of alkaline-basaltic magmas which manifested themselves in formation of the andesite-trachyandesite dike complex (age: 200-230 m. y.).

ALMADÉN DEPOSIT is situated in Spain. For the period of 2000 years about 500000 tons of metal in ores containing 10-12% Hg have been recovered. The annual mercury production is 1500-2000 tons, the average mercury content being 1.5%. The area of the deposit is composed of a sandy-shal-volcanogenic Silurian-Devonian sequence 4000 m thick. The volcanites are represented by lavas and tuffs of basalts, dolerites and quartz andesites. These are intruded by stocks of leucocratic granites (age – 320 m. y.), by dikes of dolerites, rhyolites and lamprophyres. The volcanogenic-sedimentary sequence composes a synclinal fold of the sublatitudinal strike extending for 25 km; it is complicated by transverse faults.

Ores occur as sheet-like and lenticular bodies restricted to the steeply dipping quartzite beds which are overlain by shales (Fig. 94). The thickness of a set of beds of terrigenous rocks with ore-bearing quartzites is 70 m. The length of the ore bodies along the strike is 250-300 m, their thickness varies
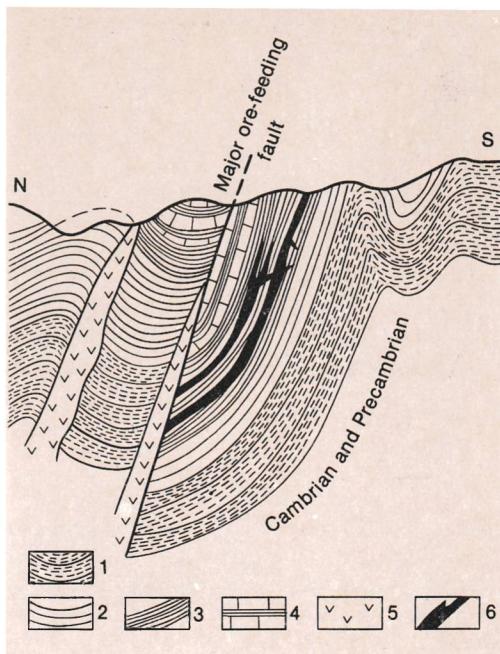
Fig. 94. Geological section of the Almaden deposit:

1-3 – Lower Silurian sediments:
  1 – sandstones;
  2 – shales;
  3 – coaly shales;
  4 – pyritized graphitic shales interbedded with Upper Silurian limestones;
  5 – dikes of diabase porphyrites;
  6 – mineralized quartzites

from 2 to 14 m, being on the average about 10 m. The ore is traceable to the depth of 400 m. The main ore mineral is cinnabar; native mercury, pyrite, chalcopyrite, pyrrhotite, markasite, galena, sphalerite and metacinnabar are subordinate; the main gangue mineral is quartz; barite, calcite, zeolite and dikkite being subordinate.

There are two points of view as to the age and genesis of the Almadén Deposit (V. Smirnov, 1978). According to the first one, the deposit was formed in the Alpine epoch from hydrothermal fluids, which, in particular, is confirmed by the presence of rich ores near the faults along which kaolinization and mercury mineralization are observed. The supporters of the second standpoint believe that the deposit was formed in the Caledonian epoch as a volcanogenic-sedimentary type with a subsequent partial transformation.

Deposits of Quartz-fluorite-antimonite-cinnabar Formation

KHAIDARKAN DEPOSIT is located in the Central Asia. The area is composed of massive and banded limestones of the Lower-Middle Carboniferous age and of Middle-Upper Carboniferous shales. They are overthrust by a sequence of Silurian shales. Ore-bearing structures are repre-
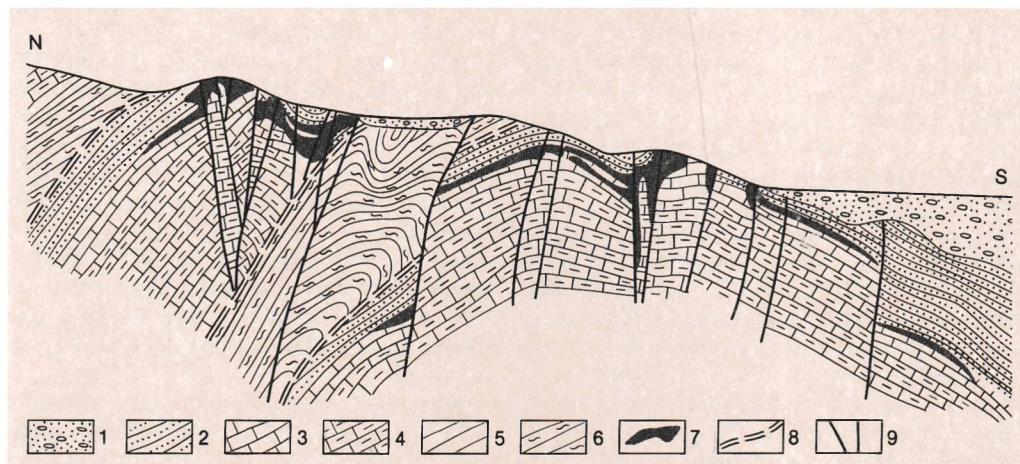
Fig. 95. Geological section of the Khaidarkan deposit. (After N. Nikiforov):

1 – Quaternary sediments;
2 – Middle Carboniferous sandstones, shales and conglomerates;
3 – Middle Carboniferous limestones;
4 – Lower Carboniferous limestones;
5 – sandstones and shales of Lower Devonian;
6 – Silurian shales and sandstones;
7 – jasperoids with cinnabar;
8 – overthrust faults
9 – faults and slip faults

sented by latitudinal anticlinal folds of the box type with gently dipping apical parts and steep limbs. These folds are complicated by longitudinal and transverse faults which serve as ore feeding conduits. Dikes of diabase porphyries are also observed.

The ore mineralization is mainly confined to breccias of jasperoids (silicified limestones). These form thick (up to 40 m) sheet-like bodies localized at the contact between the massive limestones which constitute cores of the anticlines ans overlying shales. Jasperoids develop also along the faults (Fig. 95). The ore bodies have sheet-like, lenticular, pipe-like and pocket-like configuration. They are characterized by an extremely irregular distribution of mercury that concentrates in ore columns confined to the "ore traps" (Fig. 96) formed by a combination of structural and lithological factors.

Mercury and antimony-mercury types of ores are distinguished in the deposit. The main ore minerals are cinnabar and antimonite; gangue minerals consist of quartz, fluorite and calcite; pyrite, arsenopyrite, grey ores, getchellite, livingstonite, galena, sphalerite, realgar and orpiment as well as sericite, dikkite and barite are subordinate. The ores are characterized by disseminated, mottled, pocket-like, brecciated, massive, pectinate, cockade and drusy structures and by hypidiomorphic, graphic, corrosion textures, as well as that of recrystallization.

Ore deposition occurred at a temperature interval of 285-50 °C in 3 stages: (1) quartz-fluorite-antimonite-cinnabar; (2) calcite-cinnabar; (3) realgar-orpiment. The cinnabar was deposited at a temperature lower than 135 °C. Hydrothermal alteration of the wall rocks involved silicification of limestones, sericitization and argillization of shales.
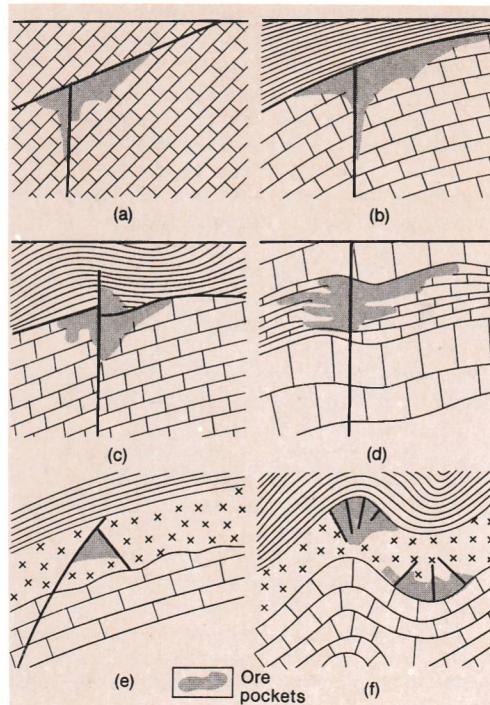
Fig. 96. Types of "ore traps". (After V. Smirnov and V. Fedorchuk):

a– in rocks of similar composition at a junction of gently and steeply dipping fissures;
b– at a junction of a steeply dipping fissure with a contact of the screening rock (shale) occurring on a more brittle basement (limestones);
c– at an intersection of the fissure with the contact of the screening rock;
d– at an intersection of the steeply dipping fissure with a set of thin-bedded limestone;
e– at the corner formed by two intersecting fissures in jasperoids;
f– in fissured bends of bed of friable jasperioids

Deposits of
Carbonate-cinnabar Formation

These are confined to limestones and dolomites being represented by conformable sheet-like bodies of the intraformational type and characterized by the simple mineral composition of the ores.

REFERENCES TO "NONFERROUS METALS" SECTION

Bowen, R., Gunatilak, A., Copper: its Geology and Economics. Applied Science Publishers, Ltd., London, 1977.

Bushinskii, G. I. Geology of Bauxites., Moscow, Nedra, 1975.

Fedorchuk, V. P. Metallogeny of Mercury and Antimony in Tien Shan. In: *Regularities in Distribution of Mineral Deposits,* Vol. 9, Moscow, Nauka, 1970.

Geology of Kuroko Deposits. Tokio, 1974.

Geology of Tin Deposits of Foreign Countries. Ed. by S. F. Lugov and M. G. Rub. Moscow, Nedra, 1969.

Glazkovskii, A. A., Gorbunov, G. I., Sysoev, F. A., Nickel Deposits. In: *Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl. Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Goretskii, Yu. K. Regularities in Distribution and Conditions of Formation of the Principal Types of Bauxite Deposits. *Trudy VIMS,* issue 5, nov. ser., 1960.

Handbook of Stratabound and Stratiform Ore Deposits. Part II, Regional Studies and Specific Deposits, Vol. 5. Regional Studies, vol. 6, Cu, Zn, Pb and Ag Deposits, p. 1–585, Elsevier, Amsterdam–Oxford–N. Y., 1976.

Hollister, V. T. An Appraisal of the Nature and Source of Porphyry Copper Deposits. Mineral Sci. and Eng., No. 7, Ro. 3, 1975.

Hutchinson, R. W. Volcanogenic Sulfide Deposits and Their Metallogenic Significance.– *Econ. Geol.,* Vol. 68, No. 8, 1973.

Khrushchov, N. A. Molybdenum.-*Trudy VIMS.* Issue 19, 1961.

Kirpal, G. R. Commercial Types of Bauxite Deposits and their Geological and Economic Evaluation, Moscow, Nedra, 1974.

Kirpal, G. R., Tenyakov, V. A. Bauxite Deposits, In: *Ore Deposits of the USSR,* Vol. 1, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Krivtsov, A. I. Types of Areas of Copper-porphyric Mineralization. In: *Geology of Ore Deposits,* No. 4, 1977.

Krutov, G. A. Cobalt Deposits. In: *Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Kuznetsov, V. A. Mercury Deposits. In: *Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl., Ed. By Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Large, R. R. Chemical Evolution and Zonation in Volcanic Terrains.– *Econ. Geol.,* vol. 72, No. 4, 1977.

Lowell, G. D., Guilbed, G. M. Lateral and Vertical Alteration.– Mineralization Zoning in Porphyry Ore Deposits.– *Econ. Geol.,* No. 4, 1970.

Materikov, M. P. Tin Deposits: In: *Ore Deposits of the USSR,* Vol. 3, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1977.

Mayer, Ch., Shi, E. et al. Ore Deposits of Butte Region in Montana State. In: *Ore Deposits of the United States, 1933-1976.* The American Institute of Mining, Metallurgical and Petroleum Engineers, Inc. Vol. II. New York, 1968.

Molybdenum Deposits (S. P. Wallas, N. K. Mooncaster, D. S. et al. In: *Ore Deposits of the USA, 1933-1967.* The American Inst. of Mining, Met. and Petrol. Engineers, Inc. V. II, New York, 1968.

Metallogeny of Mercury. Editors: V. I. Smirnov, V. A. Kuznetsov, V. P. Fedorchuk, Moscow, Nedra, 1976.

Mintser, E. F., Popova, N. N. Bismuth Deposits. In: *Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Ore Formations of Endogenous Deposits, Vols. 1 and 2, Moscow, Nauka, 1976.

Pavlova, I. G. Copper-Porphyric Deposits, Leningrad, Nedra, 1978.

Pek, A. V. Geology of the Ore Field and Deposit of Tyrnyauz – *Trudy IGEM AN SSSR,* Issue 56, 1962.

Pervago, V. A. Conditions of the Formation and Geological-economic Evaluation of Commercial Nonferrous Metal Deposits. Moscow, Nedra, 1975.

Platform Bauxites of the USSR, Moscow, Nauka, 1971.

Pokalov, V. T. Genetic Types and Prospecting Criteria of Endogenous Molybdenum Deposits, Moscow, Nauka, 1972.

Pokalov, V. T. Molybdenum Deposits. In: *Ore Deposits of the USSR,* Vol. 3, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Popov, V. S. Geology and Genesis of Copper-and Molybdenum-porphyric Deposits, Moscow, Nauka, 1977.

Prediction, Prospecting, Exploration and Geological-economic Assessment of Tungsten Deposits (a manual) Ed. by F. R. Apeltsin and N. A. Khrushchov, Moscow, Nedra, 1978.

Pyritic Deposits of the World. Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1979.

Samonov, I. Z., Pozhariskii, I. F. Copper Deposits. In: *Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Sapozhnikov, D. G. Distribution of Laterite Bauxites in the USSR. In: *Weathering Crust,* issue 12, Moscow, Nauka, 1973.

Silitoe, E. S. The Tops and Bottoms of Porphyry Copper Deposits.– *Econ. Geol.,* Vol. 68, No. 6, 1973.

Smirnov, V. I. Pyritic Deposits. In: *Genesis of Endogenous Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Smirnov, V. I., Gorzhevsky, D. I. Lead and Zinc Deposits. In: *Ore Deposits of the USSR,* Vol. 2, 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Smirnov, V. I. Ryzhenko, L. M. Some Aspects of the Formation and Distribution of Mercury Deposits. In: *Regularities in Distribution of Commercial Minerals,* Part 1, Moscow, AN USSR publishers, 1958.

Stratified Copper Deposits of the USSR, Leningrad, Nedra, 1973.

Shcheglov, A. D., Butkevich, G. V. Tungsten deposits. In: *Ore Deposits of the USSR,* Vol. 3, 2nd ed., revised and suppl. Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

Shcheglov, A. D., Tenyakov, V. A. Bauxite Deposits in Australia.– *A Review of VIEMS,* Ser. 3, 1972.

Shcherba, G. N. Creisen Deposits. In: *Genesis of Endogenous Ore Deposits,* Moscow, Nedra, 1968.

Tungsten Deposits, Criteria of Their Prospecting and Evaluation. Ed. by F. E. Apeltsin, Moscow, Nedra, 1979.

Valeton, I. Bauxites. Elsevier Publ. Company, Amsterdam, London, New York, 1972.

Volcanogenic Pyritic-polymetallic deposits. Ed. by G. F. Yakovleva, Moscow, Moscow University Press, 1979.

Yudin, I. M. Counrad Copper Deposits, Moscow University Press, 1969.

Zharikov, M. G. Antimony deposits. In: *Ore Deposits of the USSR,* 2nd ed., revised and suppl., Ed. by Acad. V. I. Smirnov, Moscow, Nedra, 1978.

RARE ELEMENTS

The elements which, owing to certain reasons (late discovery, rare occurrence in nature, the absence of demand, difficult extraction procedures, etc.) started to be used for industrial purposes only during the last decades have been termed as rare elements. These consist of more than 30 elements which are subdivided into the following groups: (1) rare alkaline elements – lithium, rubidium, cesium; (2) light elements – beryllium; (3) rare high-melting elements consisting of tantalum, niobium, zirconium, hafnium; (4) rare earths or lanthanides, and their analogues (yttrium, scandium); (5) dispersed elements accumulating mainly in sulfide ores – germanium, rhenium, thallium, cadmium, indium, selenium, tellurium.

Thus, the term "rare elements" is not directly connected with rarety of their occurrence in nature, and is a historically accepted notion. They are often called also rare metals, but since metalloids (for example, selenium) are also included in their number, the term "rare elements" is believed to be more correct.

Though the rare elements belong to different groups of the periodic system which are characterized by different behaviour in the Earth's crust, all of them are united by a single common feature – they have one or several geochemical analogues among widely abundant rock- and ore-forming elements. And the higher the geochemical affinity between them, the lesser possibility the rare elements have to form their own concentration (deposits) and more widely they will be dispersed in minerals of rock- and ore-forming elements. The rock-forming element (P) and its rare geochemical analogue (R) form a unique geochemical pair P-R (for example, K-Rb, Si-Ge, Al-Ga, Mo-Re, Ti-Nb-Ta, Ca-TR, S-Se, Zn-Cd). Concentration of a rare element is possible only in the case, when the migration routes of the widely abundant element (P) and its rare analogue (R) are separated.

18 LITHIUM DEPOSITS

Lithium was discovered in 1817 by the Swedish chemist A. Arfwedson. Last century it was used on a limited scale in medicine. Because of its unique properties – extraordinary lightness (its density being the .owermost of all metals – 0.53), great thermal capacity, extremely high reaction ability, its readiness to form alloys with Be, Mg, Al, Cu, Pb – lithium was subsequently utilized in more than 150 fields. It is used in

metallurgy, electric, ceramic and chemical industries.

Because of the development of nuclear physics it has been established that isotope ^{6}Li (7.52% of the sum of stable isotopes ^{6}Li + ^{7}Li) may serve as a source for obtaining tritium which is required to produce thermonuclear processes. Production of lithium in the capitalist and developing countries greatly increased, and in 1976 the quantity of lithium recovered (calculated in Li_2CO_3) made up 22 000 tons. In 1975 the price of 1 kg of metal of 99.99% purity was 22-25 US dollars, and one ton of the spodumene concentrate with 6% Li_2O – 72-90 US dollars.

Granite pegmatites constitute the leading type of lithium deposits. These pegmatites contain accompanying components Ta, Sn, Be, Cs, feldspar and a flotation mica concentrate. K-feldspar in them is enriched in Rb and shows a low K/Na ratio. A harmful admixture for application of lithium silicates in ceramic and glass industries is iron. High-grade ores contain 1.3-1.5, less often up to 2% Li_2O, low-grade are considered to be pegmatites that contain 0.6-1% Li_2O. Another source for obtaining lithium is represented by lithium-enriched waters such as brines in dry lake, subsurface brines, and brines of intensely evaporating water basins, as well as highly mineralized iodine-bromine oil underground waters.

The total reserves of Li_2O in the capitalist and developing countries amount to 28 million tons, of which one million tons have been measured and prepared for mining. Large lithium deposits are those containing one million – 500 000 tons, average deposits – 500-200 thous. tons, and small deposits – up to 200-100 thous. tons.

GEOCHEMISTRY AND MINERALOGY

Lithium is a lithophile "crustal" element that concentrates in acidic magmatic and sedimentary clayey rocks of the Earth's crust. Its crustal abundance (clarke) is $2.9 \cdot 10^{-3}$; its abundance in the continental crust is markedly higher ($3.3 \cdot 10^{-3}$) than in the oceanic crust ($1.9 \cdot 10^{-3}$). Concentration coefficient is about 500.

Lithium is characterized by a dual geochemical nature. Being typically an alkaline element close to Na, with which it is closely associated because of a similar size of its ionic radius (0.68 Å), lithium follows Mg in the magmatic processes, substitutes it isomorphically (according to a scheme $2Mg^{2+} \leftarrow Li^+Al^{3+}$ or $Mg^{2+}Al^{3+} \leftarrow Li^+Si^{4+}$). In all minerals it plays the role of Mg^{2+} or Fe^{2+} being with them in the same coordination. This results in formation of lithium analogues of the majority of magnesium silicates (lithium pyroxenes, amphiboles, micas, chlorites).

In the course of magmatic crystallization owing to a small value of the coefficient of distribution between the segregating solid phase and the melt the migration routes of Mg and Li are separated. Lithium accumulates in the latest differentiates of the granitic complexes and at their final stages of consolidation. Because of this, it concentrates at the latest pegmatites and at their shallow analogues ("rare metal granites"). Accumulation of lithium in residual brines during crystallization of saline systems is caused by the same reason.

Lithium is distinguished by its extraordinary fluorophylic and high chlorophylic properties, i.e. by its strong chemical affinity for chlorine and fluorine, because of which it passes, under high fluorine activity, into a fluidal phase taking part in a greisen process.

Under exogenous processes the migration routes of Li and Mg diverge, and a linkage between Li, Al and Cl becomes predominant. Lithium accumulates together with Al in clays, especially in the clays of salinized lagoons rich in chlorine.

Lithium is a constituent of 28 minerals, mainly, silicates and phosphates, but it is chiefly recovered from spodumene LiAl $[Si_2O_6]$ that contains 6-7.5% Li_2O. Approximately 80% of all lithium reserves in pegmatites are represented by spodumene ores. At the Bikita deposit in Zimbabwe the main lithium minerals – petalite LiAl $[Si_4O_{10}]$ containing 3.5-4.5% Li_2O and lepidolite $KLi_n(Fe, Mg)_m Al_p [Si_{4-q}Al_qO_{10}]$ (F, OH) (3-5.5%). Though the petalite contains lesser amounts of Li_2O than does spodumene, it is free of Fe admixture and

therefore, without additional treatment may be used to obtain ceramics. Occasionally, lithium is recovered in small quantities also from ambligonite LiAl $[PO_4]$ (F, OH) (6-9%), eucryptite LiAl $[SiO_4]$ (7-10%) and from cinnvaldite KLiAl (Mg, Fe) $[Si_3AlO_{10}]$ (F, OH)$_2$ (3-4%). All lithium minerals appear to change readily under hydrothermal and hypergene conditions, the lithium in this case is leached from them.

METALLOGENY

Lithium endogenous deposits are related to granite pegmatite fields which occur among the rocks of the cordierite-amphibolite metamorphic facies and are confined to the extended linearly elongated geosynclinal troughs within ancient shields (proto-geosynclines) and to Phanerozoic folded geosynclinal regions. The earliest (3.0-2.8 b.y.) large fields of lithium-bearing pegmatites were formed in the period when narrow junction downwarps (geosynclinal troughs) filled in with terrigenous-volcanic rocks interbedded with sheet-like bodies of basic rocks started to develop in protoplatforms still having a thin sialic crust. The granite-gneiss cupolas developed in the bottoms of these troughs, and bed-shaped bodies of parent granites were extending from the cupolas along the side faults.

Lithium pegmatites localized in the upper stage of trough complexes, among the rocks of the cordierite-amphibolite facies, are usually restricted to massifs of basic rocks. The pegmatite deposits are located rather far from the parent intrusive bodies and often do not exhibit a spatial link with the latter. Such geological setting have, for example, the largest deposits of Canada (Litia, La Croix, La Corn, Quebec, Ontario and others), Zimbabwe (Bikita) and Australia (Londonderry and others).

In the Phanerozoic time lithium concentrated, besides permatites, also in micas of rare metal granites and in greisens. Their development is related to the period of emplacement of granitic batholiths at the middle stage of the geosynclinal cycle, and particularly, to late geosynclinal and post-geosynclinal stages of emplacement of hypabyssal granite stocks. In the first case they form belts occurring along the median uplifts which comprise median massifs, and in the second case the location of pegmatite belts is controlled by post-folding faults. During the Hercynian time spodumene deposits of the North Caroline (King's Mountain, Bessemer City and others) were formed being part of the gigantic pegmatite belt of the Appalachians. The youngest, Alpine pegmatite fields carrying lithium mineralization have been revealed in Afghanistan.

Based on a number of geologic factors and on the data of isotopic ratios of $^{87}Sr/^{86}Sr$, the granite complexes to which lithium deposits are related, should be considered as crustal palingenetic allochthonous complexes.

In Cenozoic lithium concentrated mainly in various mineralized waters.

TYPES OF COMMERCIAL DEPOSITS

Commercial deposits of lithium belong to pegmatites and to mineral waters.

In the last few years high Li_2O concentrations (0.5-1%) have been detected among Paleozoic acidic effusives in ring depressions which are filled with fluorine-rich carbonaceous-carbonate shales where lithium is mainly contained in micas.

PEGMATITIC DEPOSITS

A. Fersman attributes lithium pegmatites to the sodium-lithium type. With respect to morphological features, composition and internal structure three types of lithium pegmatite deposits are distinguished.

1. Steeply dipping extended branching veins predominantly of the spodumene-albite composition with poorly expressed zonality and the spodumene content of 15-25%. This is the most important type of lithium deposits which apart from spodumene also contains Ta_2O_5 (0.005-0.01%), BeO (0.04-0.07%), SnO_2 (0.03-0.08%).

Deposits are represented by swarms of parallel branches of steeply dipping linear
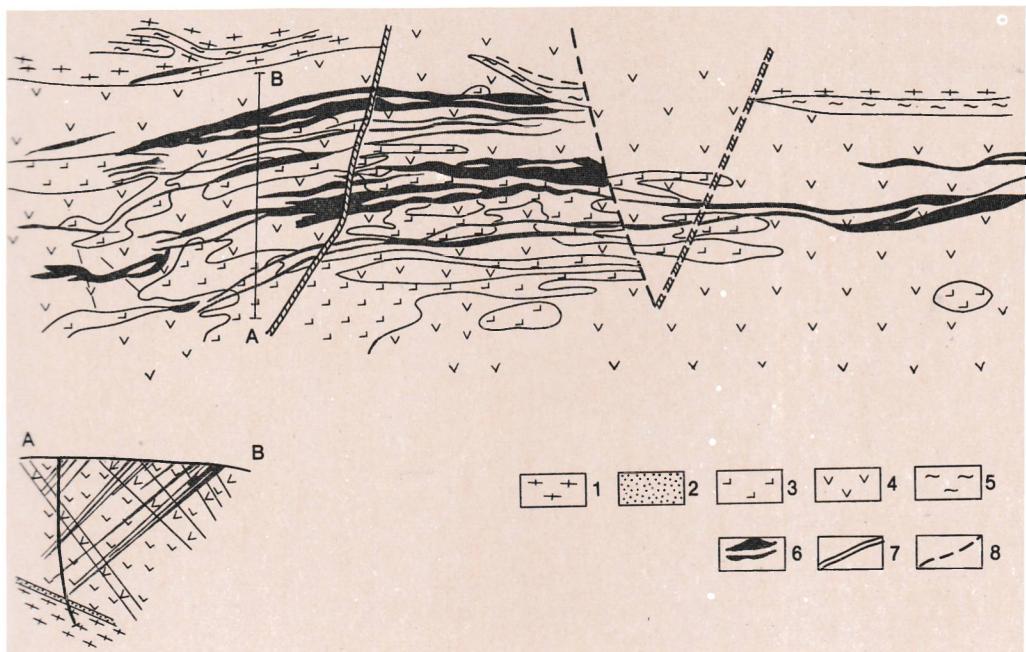
Fig. 97. Geological sketch map of a spodumene deposit represented by steeply dipping vein branches. (After S. Evenchik):

1 – Archean gneiss-granites;
2-6 – Lower Proterozoic rocks:
  2 – conglomerate bed;
  3 – gabbro-anorthosites;
  4 – amphibolites;

5 – talc-chlorite schists;
6 – pegmatites;
7 – diabase dikes;
8 – faults

veins extending for a distance from 1-3 to 15-20 km and more along the regional fault zones (Fig. 97). Their thickness varies from 0.5-1 to 20-25 m and a vertical span of the spodumene mineralization – from 3 to 3.5 km (Rossovskii, L., 1976).

The host rocks in the Precambrian troughs are represented by para- and orthoamphibolites, gabbro-anorthosites, biotite gneisses, and in Phanerozoic geosynclines – by sandy-shale sequences, very rarely by marbles metamorphosed at the cordierite-amphibolite facies.

A fringe of fine- and medium-grained pegmatite is observed at the contact of pegmatites which further changes for microcline-quartz-albite-spodumene pegmatite. The size of microcline and spodumene segregations in the latter tends to increase, and reaches frequently 0.5-1.5 m. Typical of these segregations is directional arrangement of microcline blocks and, especially, of spodumene crystals which are located

somewhat perpendicular to the contacts. For pegmatites occurring in tectonically active areas banded and patch-like structures are typical (Fig. 98).

In cases when a vertical span of spodumene mineralization is considerable a vertical zonality may develop. Accumulation of fluorine in apical parts of pegmatite branches lead to an appearance of amblygonite, lepidolite and to an increase of Ta and Cs content. At lower portions of the branches a drop in the content first of Ta and then of Li may be observed.

Around spodumene pegmatites wide halos of relatively high lithium concentrations and less intensive though more contrast cesium halos (particularly in pegmatite containing relics of replaced pollucite) are developed. Where spodumene pegmatites occur in amphibolites, along their contacts, a local development of tourmalinization and biotitization (more widely) is observed. Biotite here contains 6-8% Cs_2O, and
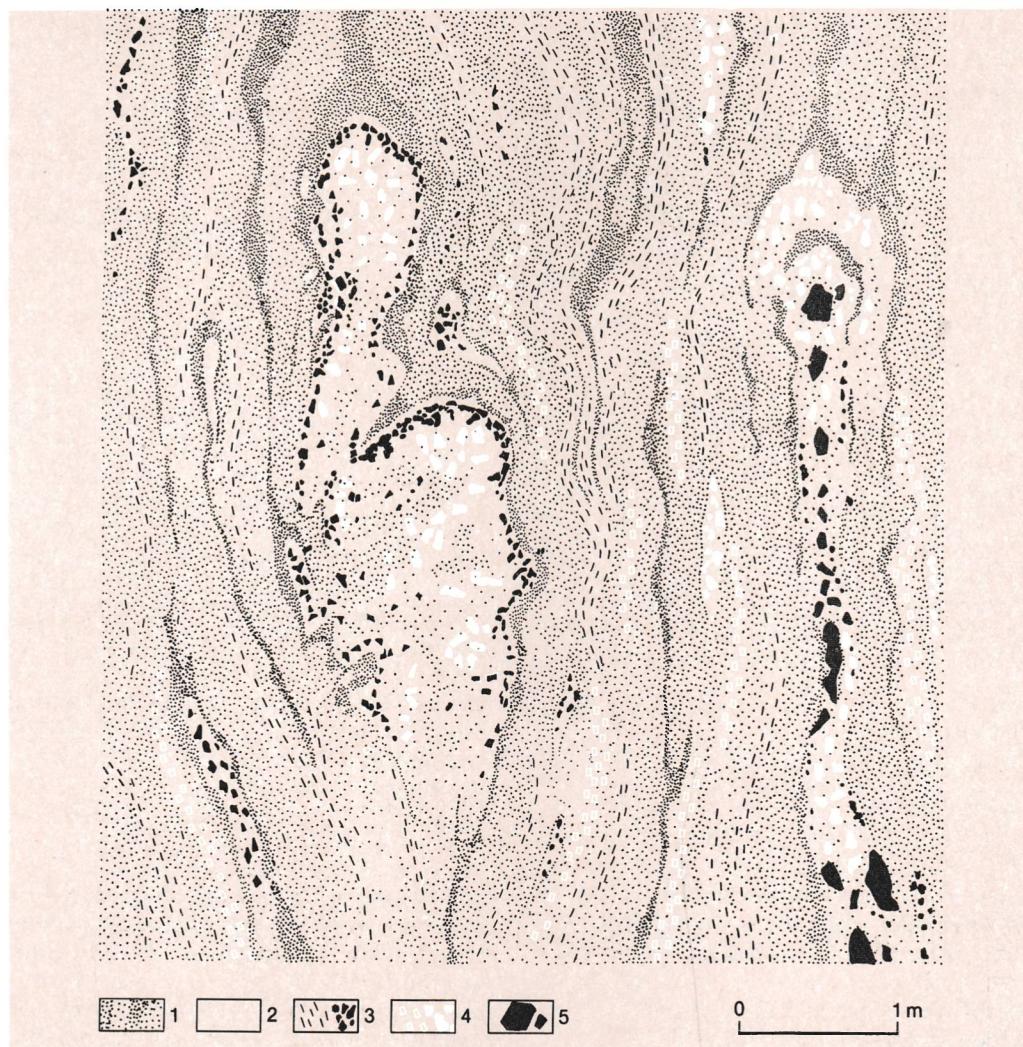
Fig. 98. Banded and local structures in pegmatites formed in active tectonic environment. (After I. Nedumov):

1—banded quartz-albite aggregate (fine- and coarse-grained);
2—quartz;
3—tourmaline;
4—spodumene;
5—microcline

holmquistite (lithium amphibole) is also formed.

In the crust of weathering all spodumene is easily converted into clay minerals.

Examples of this type of deposits may be found in the North Caroline State, the USA (Alexander County and others), Quebec, Canada (Lithia, La Corn massif), Spain (Lalín), Afghanistan (Drumgal, Djamanak, Pasgushta and others) and also in the USSR.

2. Gently dipping zonal bodies of the microcline-spodumene-albite and microcline-petalite-albite composition contain Ta, Cs, Li and Be. They are of interest as promising tantalum and cesium deposits which are distinguished by almost horizontal setting and by a stage-by-stage arrangement of pegmatite bodies. The upper bodies carry essentially tantalum mineralization, whereas the lower ones contain lithium minerals. Petalite is often

present in large quantities and in many instances is decomposed into an aggregate of spodumene and quartz ($LiAl[Si_4O_{10}] \rightarrow$ $\rightarrow LiAl[Si_2O_6] + 2SiO_2$); also observed are lepidolite, occasionally amblygonite and eucryptite. This type of deposits can be exemplified by the Bernik-Lake (Tanco) deposit in the Manitoba Province (Canada), Bikita Deposit (Zimbabwe) and a number of pegmatite fields in the USSR.

3. Thick steep pipe- and stock-shaped, and lenticular fully differentiated bodies of the microcline-spodumene-albite composition with Ta, Be and Cs are characterized by an extremely irregular distribution of mineralization (in the form of pockets), and by the development of gigantic spodumene crystals reaching 15 m in length in the central parts of these bodies. These include the pegmatites of the Black Hills (Etta Mine, Fig. 99; Pirless and others) in Southern Dacota (the USA) and some pegmatite deposits in China.

There is no unified opinion concerning the genesis of lithium mineralization. V. Nikitin [1968], V. Gordienko [1970] and some other scientists believe that all spodumene was metasomatically formed in the process of alteration of aplites or quartz-microcline pegmatites caused by hydrothermal solutions containing sodium and lithium. K. Vlasov [1955], A. Ginzburg [1955, 1959], N. Solodov [1962], L. Rossovskii and others assume, like A. Fersman, that the main bulk of spodumene was formed by crystallization of the residual melt (solution) enriched in Na and Li.

The following physico-chemical factors must be taken into account when considering the genesis of these pegmatites:

(a) lithium, like fluorine and sodium, causes a sharp decrease (down to 550 °C) of the temperature of granite crystallization;

(b) investigations performed on the synthesis of spodumene have indicated that without admixtures it may be formed only under high pressure (over 5000 kgf/cm^2). At the same time, petalite without admixtures is crystallized at lower pressures;

(c) according to the data on homogenization of fluid inclusions, spodumene forms at a wide range of temperatures – from 580 to 220 °C. Almost the same data (from 480 to 430 °C) have been obtained on microcline, which is paragenetically related to spodumene, using the Barth geothermometer (V. Gordienko, 1970).

Thus, the spodumene pegmatites are formed from the rather low-temperature melt; at the first stages crystallization occurs from the melt (near-contact zones), then from the supercritical and hydrothermal solutions.

MINERAL WATERS

About 60% of the reserves of lithium are related to mineral waters. Several types of lithium-rich waters are distinguished.

1. Intercrystalline brines of dry salt lakes. An example is the Sirls dry lake in California (the USA) that occupies an area of 70 km^2 and is filled with a salt-bearing sequence (halite, natron, mirabilite) of 15-25 m thick. Using boreholes and pumps the brine containing 0.015% Li_2O is extracted from this sequence. Lithium occurring as $Li_2Na[PO_4]$ is precipitated from the brine with the aid of phosphorites.

2. Brines of drying water basins (lakes, lagoons, bays and seas). Such are waters of the Great Salt Lake in the Utah State (the USA) (0.013% Li_2O), Dead Sea (0.004% Li_2O), drying lakes (salars) in the Atacama Desert (Chile) which reveal extremely high lithium concentrations (0.2%).

3. Underground rich brines. The Clayton Valley Deposit in the Silver Peak Range (Nevada state, the USA) may serve as a good example. The brines containing 0.08% Li_2O are confined to clastic sediments among thick andesite and rhyolite lava flows overlain by alluvium.

4. Underground waters of oil and gas deposits in marginal and intermontane basins of platform regions, which are commonly restricted to intersalt and subsalt water horizons of oil structures. These waters are of the sodium-calcium-chloride type. They contain, apart from Li_2O (up to 0.08%), also Rb, Cs, I, Br, B and Sr.

5. Thermal waters of regions of the present-day active volcanism are also rich in lithium, and a generally low salt content of these waters favours its extraction.
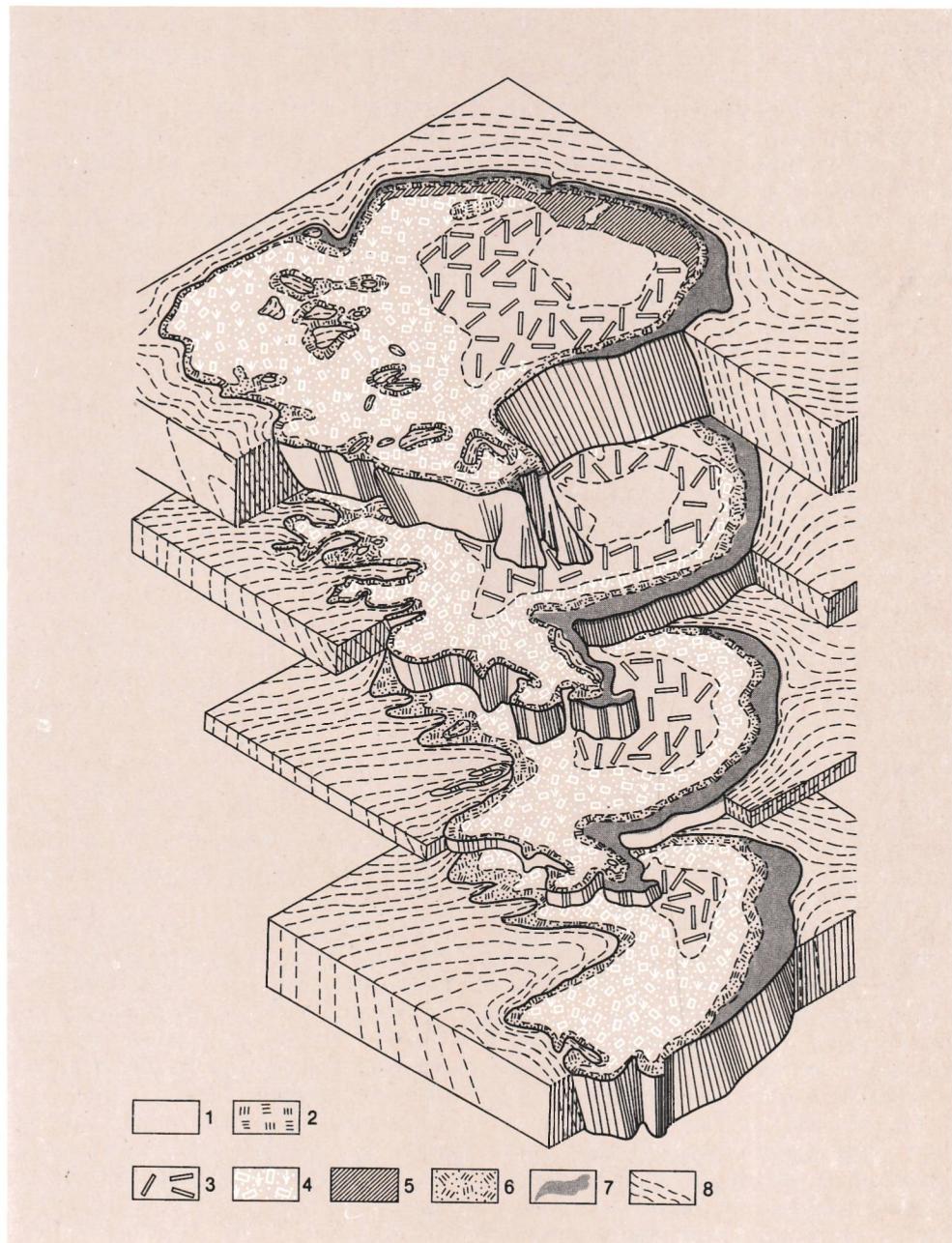
Fig. 99. Etta Mine pegmatite body in Black Hills, South Dacota (USA). (After I. Nedumov):

1 – quartz core with spodumene crystals along the periphery;
2 – muscovite-quartz segregations with miarolitic cavities;
3 – quartz-spodumene zone;

4 – spodumene-quartz-cleavelandite zone with cassiterite, tantalite, beryl;
5 – spodumene-quartz-microcline zone with beryl;
6 – albite-muscovite-quartz zone with beryl;
7 – quartz-microcline zone with oligoclase-albite;
8 – metamorphic schists

19 CESIUM AND RUBIDIUM DEPOSITS

Cesium and rubidium were first detected by a spectral analysis by R. Bunsen (rubidium in 1859) and R. Bunsen and R. Kirchhoff (cesium in 1860). For a long time these elements remained to be of no practical use. Thanks to the unique properties of cesium, consisting in the largest (of all cations) size (0.165 nm), the lowermost ionization potential (3.89 eV) and in the low level of electron work function (1.87 eV), it becomes, when exposed to the sun or cosmic rays or when heated, a source of an electron flux. This is the property on which the production of photoemissive cells, photoelectron multipliers, electron-optical transducers and solar batteries is based. Application of cesium as fuel in ion rocket engines for space flights, and for improving the work efficiency of plasmic generators, i.e. of direct transformation of thermal energy into electric one in magnetohydrodynamic (MHD) generators and thermoelectron transformers (TET), is gaining at present great importance. All this has given a great impetus to a rapid growth of its production – from a few tens of kilograms to first tons. It is believed that by the end of this century the world production of cesium (without the socialist countries) will amount to 30 tons. Rubidium is used on a limited scale in medicine and in analytical chemistry. The inferred requirement for rubidium by the end of this century will be about 3 tons. In 1976 a price of one kg of cesium was 900-1 000 US dollars, while one ton of pollucite concentrate – 300 US dollars. The world production is based on pollucite ores of pegmatite deposits containing from 0.3-0.5 to 2-3% Cs_2O. In the lump sorted ore concentrates the Cs_2O content is not lower than 20%. Unique deposits comprise over 100 thous. tons of Cs_2O, large deposits – a few thousands of tons, average deposits – hundreds of tons, and small deposits – tens of tons.

Being typically lithophile, both elements concentrate in end differentiates of the granitic palingenic complexes. The Cs crustal abundance (clarke) is $3.7 \cdot 10^{-4}\%$,

and that of $Rb - 1.5 \cdot 10^{-2}\%$. Their average contents in different rocks (in $1 \cdot 10^{-4}\%$) are: 0.1 (Cs) and 2.0 (Rb) in ultrabasic rocks, 1.0 and 45 in basic rocks, and 5 and 20 respectively in acidic rocks. The concentration coefficient of cesium is up to 80 000 and that of rubidium – 20. Such a sharp difference in their concentration coefficients is one of the most striking features of their geochemical history.

Potassium is a petrogenic analogue of cesium and rubidium, but since an ionic radius of rubidium (0.149 nm) is much closer to that of potassium (0.133 nm) than the cesium radius (0.165 nm) rubidium is fully dispersed in potassium minerals and accumulates only at final stages of crystallization in rare-metal granite pegmatites entering the composition of microcline, rubidium muscovite and lepidolite (up to 3-4.2% Rb_2O). However, because of the large size of its ion, cesium enters only into the composition of minerals that possess a favourable (for this purpose) structure (micas, beryls). Therefore, it accumulates in residual solutions and forms its own mineral called pollucite (Cs, Na) $[AlSi_2O_6] \cdot nH_2O$ (30-34% Cs_2O).

Cesium readily combines with boron and fluorine into complex compounds of the $Cs[BF_4]$ type, and in this particular form it is migrating. Among sublimates of certain volcanoes a mineral called avogadrite (K, Cs) $[BF_4]$ occasionally is observed. Owing to volatility of Cs with boron and fluorine halos of comparatively high concentrations of these elements are formed around the masses of rare-metal granites and pegmatites. When lithium pegmatites are emplaced in amphibolites and are formed in an active tectonic environment tourmalinization and biotitization processes develop at their contacts; in this case biotite thus formed contains up to 6-10% Cs_2O. As a result exocontact altered rocks, up to a few tens of metres thick, contain up to 0.1-0.3% Cs_2O and may serve as a source for extraction of cesium.

In alkaline granites, syenites and at their exocontact zones accumulation of minerals of the astrophyllite group carrying up to 1.5-2% Cs_2O is observed. Cesium kupletskite is detected in pegmatites of the alkaline granites (up to 10% Cs_2O).
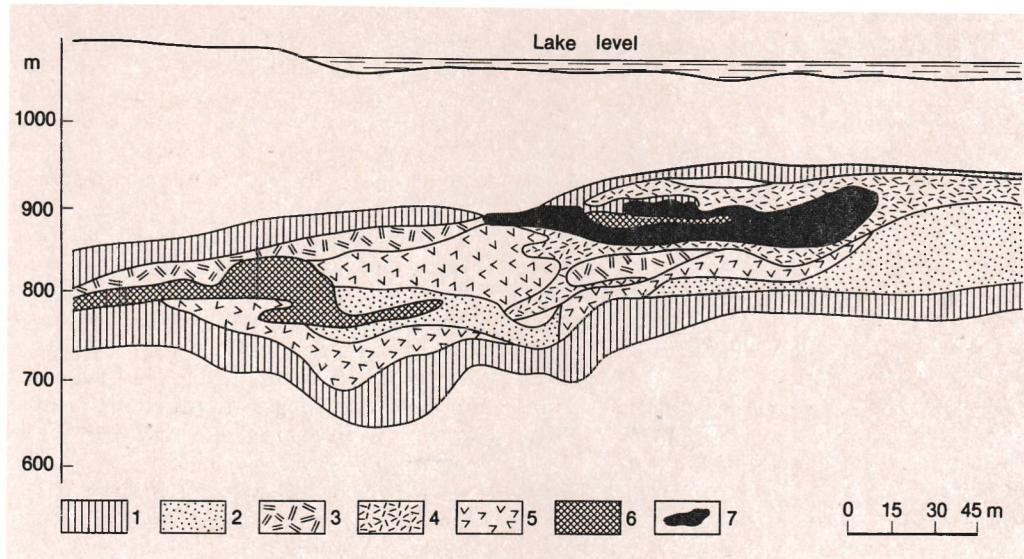
Fig. 100. Vertical section of the Tanko pegmatite body (Bernik-Lake Deposit, Canada). (After P. Chernii and R. Ferguson):

1 – albite-quartz-microcline zone;
2 – fine-grained quartz-albite zone;
3 – microcline-albite-quartz-spodumene zone;
4 – spodumene-quartz-amblygonite zone (with petalite);

5 – microcline-albite-quartz zone (with tantalum mineralization);
6 – quartz zone;
7 – pollucite zone

Cesium enters into the composition of acidic and intermediate volcanic glasses, perlites (up to 0.5% Cs_2O). Here a direct link between the cesium and H_2O contents is observed. Volcanic glasses are to be most enriched in cesium near tectonic zones, which suggests later supply of cesium to glasses.

Under exogenous processes cesium and rubidium accumulate together with potassium in salt-bearing rocks; rubidium is part of sylvite and carnallite, and cesium is absorbed by muds or is preserved in waters.

Practically all cesium is extracted from pollucite and is obtained as a by-product in a process of treating the lepidolite and spodumene concentrates. Potential sources for obtaining cesium are exocontact metasomatites with cesium biotite and volcanic glasses. Rubidium is a by-product in a process of treating the potassium salts and lepidolite concentrates.

All the cesium deposits belong to the formation of rare-metal pegmatites. They are complex and apart from cesium contain also Ta and Li, in lesser amounts Be and Sn (see "Lithium Deposits").

BERNIK LAKE DEPOSIT is a unique one being located in the Manitoba Province (Canada). It occurs among metamorphosed sedimentary-volcanogenic Lower Proterozoic rocks (2 600 m. y.) of the "Rice Lake" Group represented by amphibole-plagioclase schists intruded by granites (2 000 m. y.). The deposit has a multi-stage structural pattern. The major pegmatite body lies at 900-1 000 m above the granitic massif. It is represented by an ellipsoidal (in plan) body of the latitudinal strike that dips at angles of 10-30° in all directions and thus forming a kind of arch-like structure. The length of the body is over 1 100 m (it plunges under Bernik Lake), its width 460 m and thickness – up to 85 m. Under the major body lies a second one.

The body exhibits a distinct zonal structural pattern (Fig. 100) with a well developed quartz core. The central portion comprises a pollucite zone which consists of three lenses each up to 5 m thick. These zones are composed solely of pollucite. The Cs_2O content in them reaches 28%. The measured ore reserves make up 270 thous.

tons with the average Cs_2O content being 20.4%. The total reserves are estimated at about 200 thous. tons of Cs_2O. The deposit is unique also with respect to the tantalum content (4 300 tons of Ta_2O_5, its content 0.23%) and to rather high lithium (2.2-2.4% Li_2O). Some 90% of the world cesium production and 30-40% of tantalum production are attributed to the Bernik Lake deposit.

20 BERYLLIUM DEPOSITS

Beryllium was discovered in beryl in 1798 by the French chemist L. Vauquelin. Pure metal was obtained by P. Lebeau only after a century had passed since the discovery of the element.

Beryllium is distinguished by a considerably low density (1.847 g/cm^2), great hardness (100-150 kgf/mm^2), high elasticity (elasticity modulus of 30 000 kgf/cm^2) and heat capacity. The lowest capture section of thermal neutrons (0.009 barn) makes beryllium useful in nuclear technology. Beryllium is an ideal material for construction of aircrafts, rockets and spaceships. It is also utilized in gyroscopic instruments and in navigation and orientation systems in aircrafts, ballistic missiles, spaceships and submarines. Alloys of beryllium with Cu, Zn, Pb and Sn are widely used for creation of non-sparking melts, and with Al and Mg–for specialized superlight alloys. Beryllium is utilized as an alloying admixture in certain types of steel and as coating material for various articles (beryllization).

Production of beryllium concentrates containing 10% BeO increased from 1 000 tons in 1940 to 10-11 thous. tons in 1975. A price of one ton of beryllium concentrate was raised from 24-29 US dollars in the pre-war period to 290-300 US dollars in 1975. The price of metallic beryllium (high purity bars) in 1974 was 165 US dollars for a kilogram.

The most important beryllium-bearing deposits are granite pegmatites, from which beryllium is mainly recovered together with muscovite, tantalum and lithium minerals, and greisens, quartz-vein deposits (by-products are W, Mo, Bi), phenakite-bertrandite-fluorite metasomatites, as well as bertrandite-bearing effusives (fluorite is extracted as a by-product). Harmful admixture (when beryllium is used in atomic technology) is represented by rare earths which are characterized by a high capability to absorb neutrons.

The resources of beryllium estimated in the capitalist and developing countries were 1 200-1 500 thous. tons of BeO, more than half of which are accounted for by low-grade ores (pegmatites) containing 0.04-0.06% BeO. A unique deposit, Spor Mountain, in the Thomas Range, Utah, USA, consists of altered effusive rocks with bertrandite mineralization. The reserves are 200 thousand tons of BeO.

Beryllium deposits are considered to be large ones if they contain 100-40 thous. tons of BeO, and as ordinary if the reserves are 40-10 thous. tons. Ores containing 0.5% BeO and more are categorized as high-grade, and those containing 0.04-0.1% as low-grade.

GEOCHEMISTRY AND MINERALOGY

Beryllium has only one stable isotope, ^9Be. Isotopes ^7Be and ^{10}Be are produced in nuclear reactions under the action of cosmic rays. Beryllium is a lithophile element. It concentrates in association with palingenetic granite, alkali granite and nepheline-syenite magmas. The crustal abundance (clarke) of beryllium is $3.8 \cdot 10^{-4}$%. The average beryllium contents of different classes of igneous rocks are (in $1 \cdot 10^{-4}$%) 0.2 in ultrabasic, 1.4 in basic, 1.8 in intermediate, and 5 in acid rocks. Ore-productive intrusive rocks contain more than $5 \cdot 10^{-4}$% BeO. The concentration factor is ~ 400 for beryllium relative to its crustal abundance.

Beryllium has no direct geochemical analogues among the rock-forming elements, however, according to its geochemical properties, beryllium stands close to Si^{4+} and Al^{3+}. Despite the fact that its ionic radius (0.34 Å) is near that of the silicon ion (0.39 Å) they only display a very limited isomorphism according to the following schemes: $Na^+Si^{4+} \leftarrow TR^{3+}Be^{2+}$ (oligoclase), $2Ca^{2+}Si^{4+} \leftarrow 2TR^{3+}Be^{2+}$ (garnet,

vesuvian), $Mg^{2+}Si^{4+} \leftarrow Ti^{4+}Be^{2+}$ (pyroxenes, amphiboles). Beryllium is similar to Al^{3+} in ionic potential and electronegativity. Be^{2+} is able to substitute a small amount of Al^{3+} only if the latter is in the tetrahedral coordination according to the following schemes: $2Al^{3+} \leftarrow Be^{2+}Si^{4+}$ (muscovite, margarite), $K^+Al^{3+} \leftarrow \leftarrow Ba^{2+}Be^{2+}$ (microcline), $Na^+Al^{3+} \leftarrow \leftarrow Ca^{2+}Be^{2+}$ (oligoclase), etc. Consequently, beryllium is dispersed in rock-forming minerals in insignificant amounts and concentrates to form its own minerals which amount to 55 in number. Beryllium is characterized by a double geochemical nature: under some conditions (in acid environment) it is associated with silicon, and under the others (in alkali environment) with aluminium being able to substitute the latter in the tetrahedral coordination to produce beryllium silicates, e.g. $Na_2[BeSi_2O_6]$ – chkalovite.

Beryllium is a typical fluophile element. It forms with F and CO_3 easily soluble, stable and volatile compounds, like $[BeF_4]^{2-}$, $[BeF_3]^-$, $[BeF_2]^0$, $[Be(CO_3)F]^-$, and $[Be(CO_3)_2]^{2-}$, which are readily hydrolyzed with increasing alkalinity and temperature to form $[BeF(OH)]^0$, $[BeF(OH)_2]^-$, $[Be(OH)_2]^0$, and $[Be(OH)_3]^-$. It is in the form of these compounds that beryllium migrates. Fluorine acts as an extractor in the separation of fluid from a granite melt and removes beryllium facilitating its concentration in supercritical and hydrothermal solutions. Ore is formed as a result of decomposition of complex compounds promoted by changes in pH, pressure and temperature and by the interaction with the enclosing rocks.

Because of its low combined distribution coefficient beryllium concentrates in residual liquids during fractional crystallization of a magma exhibiting two tendencies in its behaviour: it may be dispersed crystallochemically in rock-forming minerals as a result of ionic substitution, or it may be removed into a gaseous phase coexisting with the melt as a result of the formation of its volatile compounds. Which of the two tendencies will prevail depends on fluorine activity, hydrostatic pressure (depth of for-

mation), alkalinity of the rocks, and other factors. So, beryllium either concentrates in granite pegmatites, or is removed together with flourine and concentrates in greisen or hydrothermal formations.

Under exogenous conditions beryllium is closely associated with aluminium and concentrates in clay in insignificant amounts.

As mentioned above, 55 minerals of beryllium are known, which include silicates and aluminosilicates (approximately 50% of the total), phosphates (25%), oxides and borates. In the last years new exogenous minerals of beryllium have been discovered, which are formed in oxidized zones. These are phosphates (moraesite, glucine and uralolite) and arsenates (bearsite). Minerals of commercial importance are beryl $Be_3Al_2[Si_6O_{18}]$ containing 10-12% BeO, phenakite $Be_2[SiO_4]$ (40-44% BeO), bertrandite $Be_4[Si_2O_7](OH_2)$ (40-42% BeO), helbertrandite $Be_4[Si_2O_7](OH)_2 \cdot nH_2O$ (34% BeO), chrysoberyl $Al_2[BeO_4]$ (18-20% BeO), barylite $BaBe_2[Si_2O_7]$ (16% BeO), genthelvite $(Zn, Mn)_4[BeSiO_4]_3S$ and helvite $(Mn, Fe)_4[BeSiO_4]_3S$ (12-13% BeO). Less important ore minerals are euclase $Al_2Be_2[SiO_4]_2(OH)$ (16-17% BeO) and leucophane $CaNaBe[Si_2O_6]F$ (10-12% BeO). Beryl accounts for approximately 75% of the world's resources of beryllium, though the richest beryllium ores (0.5-1% BeO) are phenakite-bertrandite, helbertrandite, genthelvite and barylite.

METALLOGENY

Economic beryllium deposits were formed during an intermediate and late phases of a geosynclinal cycle, and during periods of tectonic and igneous reactivation of platform areas in connection with acid and alkaline magmatism. An evolution can be observed in formation of different types of beryllium deposits during the geologic time. The predominant types of deposits that appeared in the Proterozoic time were beryllium-bearing pegmatites localized in narrow joint-type structures like geosynclinal troughs within ancient schields. Pegmatite fields and fault-related feldspathic metasomatites bearing genthelvite and phenakite mineralization were formed in

areas of Middle and Late Proterozoic proto-activation. Along with pegmatites, various skarn-greisen, greisen and quartz-vein deposits were formed in the Caledonian and Hercynian epochs. In the Kimmerian epoch, in connection with the reactivation of consolidated fold areas and accompanying subalkaline magmatism, phenakite-bertrandite-fluorite ores were deposited in depressions formed along fault zones. And finally, fluorite- and topaz-bearing rhyolites and their tuffs carrying helbertrandite mineralization were formed in the course of reactivation of stable structures in the Alpine epoch.

TYPES OF COMMERCIAL DEPOSITS

All beryllium deposits are endogenous. They can be divided into five economic categories: (1) pegmatitic; (2) feldspathic metasomatites; (3) greisen; (4) plutonogenic hydrothermal; and (5) volcanogenic hydrothermal.

PEGMATITIC DEPOSITS

This is the most common type of beryllium deposits which until now accounted for the total world production of beryllium. The occurrence of large crystals of beryl often reaching a few tons in weight permits them to be recovered by hand picking. Thus, 10% BeO concentrates can be derived without any ore processing. Beryl is extracted from pegmatites predominantly as a by-product when they are mined for muscovite, tantallum, cesium or lithium. Accordingly, one can distinguish rare-metal-mica-bearing (beryllium-muscovite) pegmatites and rare-metal (lithium-cesium-tantallum and lithium) pegmatites. The former are found in India, Brazil and the USA. They are localized in the apical portions and at the margins of mica-bearing and the most deep-seated rare-metal pegmatite fields; they are usually of Middle and Upper Proterozoic age; the enclosing rocks are commonly metamorphosed up to a kyanite-amphibolite facies.

A spatial relationship of pegmatites with granites is not always obvious. Commonly, pegmatites have a lenticular form and a typ-

ical concentric zonation with cores of quartz sometimes of pink colour in central parts of pegmatite bodies. The largest size of the dykes is 750 by 100 m (usually 100 to 200 by 20 to 30 m), and the thickness up to 20 m. Large crystals of beryl are localized at the margins of quartz cores, or in large-block and pegmatoid zones. According to their composition, pegmatites can be classified into quartz-oligoclase-microcline and quartz-microcline ones with a well developed quartz-muscovite replacement assemblage and poorly manifested albitization. Beryl often occurs together with black tourmaline, columbite, and cyrtolite. Occasionally uraninite and monazite accompany it.

The characteristic of beryllium-bearing rare-metal pegmatites is also given in chapters entitled "Lithium Deposits", "Cesium and Rubidium Deposits", and "Tantalum and Niobium Deposits".

DEPOSITS OF FELDSPATHIC METASOMATITES

Beryllium-bearing feldspathic metasomatites appeared in ancient shields within long-living zones of old crustal faults. The enclosing rocks, ancient granites, gneisses, basites and effusives, are intensely shattered, gneissic and sometimes mylonitized. During a later period of reactivation the rocks were subject to intense microclinization and to some albitization and greisenization. The basic rocks underwent amphibolization and biotitization. Ore mineralization related to irregular bodies of microclinites, quartz-microcline, quartz-albite-microcline rocks and even albitites were formed at the intersections of such zones with the branching faults (Fig. 101). Ore bodies are represented by irregular and intermittent series of branching flat-lying and steeply dipping echelon-like veins and lenses extending for hundreds of metres and having a thickness of a few metres. The BeO content is as high as 0.5%. No genetic ties of the ores with surrounding intrusive rocks have been established. The ore consists of genthelvite and more rarely of phenakite. Fluorite, cryolite with late alumofluorides developed after it, cyrtolite, cassiterite and
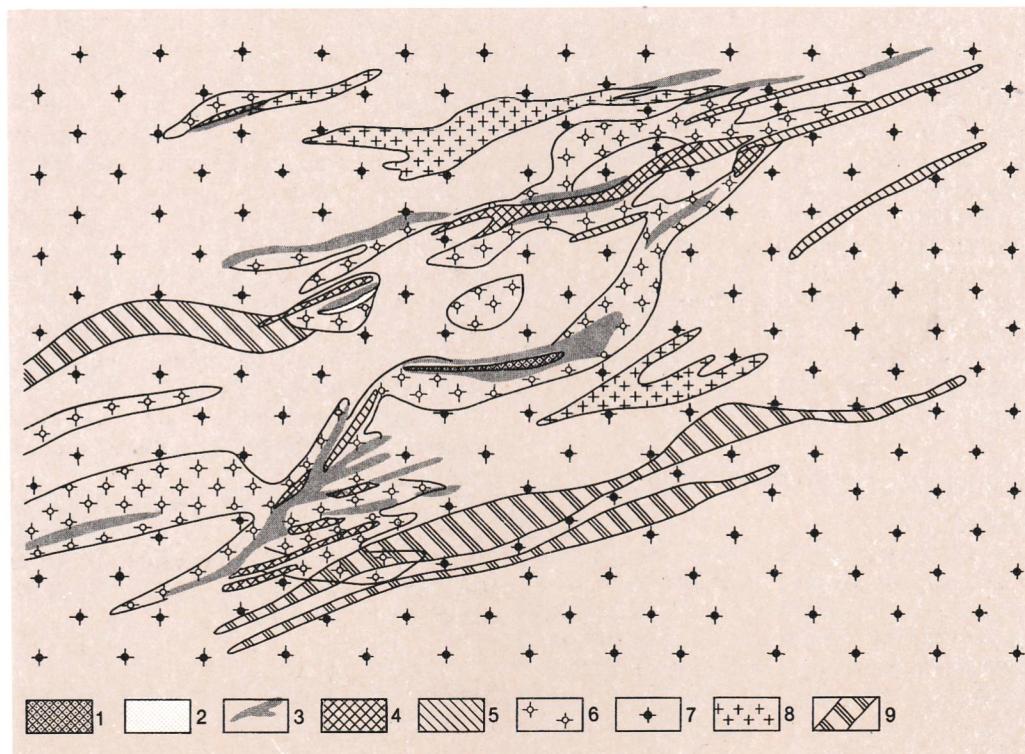
Fig. 101. Geological structure of a portion of a beryllium-bearing feldspathic metasomatite deposit. (After S. Yakovenko):

1 – albite-feldspar metasomatites;
2 – quartz-siderophyllite greizens;
3 – mica-feldspar metasomatites;
4 – feldspathic metasomatites;
5 – quartz-feldspathic metasomatites;

6 – granite with augen segregations of blue quartz;
7 – gneissoid "granite";
8 – fine-grained granite;
9 – ore bodies projected to the ground surface

willemite are usually present. Less common are sulfides.

Where metasomatic processes are developed after diabase and gabbro-diabase dykes, essentially quartz-amphibole-albite or quartz-biotite-albite rocks and occasionally albitites appear. These rocks are enriched in leucophane and bastnäsite; more rarely they contain phenakite, helvite or bertrandite.

Beryllium-bearing fenites have been found so far only in one deposit, *Seal Lake* (Labrador, Canada). It consists of bed-like bodies of alkaline syenites intruding interbedded slates and porphyric volcanic rocks of the Grenville Series. At the exocontacts of the alkaline syenite bodies and farther outward, the enclosing rocks are transformed to fenites – feldspathic metaso-matites – enriched in aegirine, arfvedsoni-te, albitite and carbonates. The latter include fine grains and veinlets of ba-rylite. Eudidymite, niobophyllite, eudialyte, neptunite and pyrochlore are present. The BeO content varies within 0.4 to 0.7%. The resources are 15 thousand tons of BeO.

GREISEN DEPOSITS

Beryllium deposits of this type are related to the apical parts of granite domes which were formed at moderate or shallow depth. They are localized in the granites themselves or, more frequently, in the rocks above them, being represented by stockwork or vein bodies. Vertical zoning is often observed in the mineralization: beryllium ore lies above the domes of rare metal tantalum-bearing
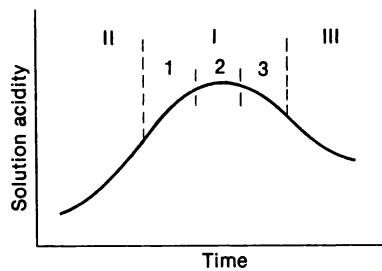
Fig. 102. Phases of greisenization (I) in relation to albitization (II) and beresitization (III). (After I. Kupriyanova).

Greisenization phases:
  1 – early deposition;
  2 – acid leaching;
  3 – late deposition

granites and grades upwards into tin- and tungsten-bearing greisens. Greisen deposits commonly contain between 0.08-0.1 and 0.2-0.3% BeO.

Beryllium mineralization may be associated both with metasomatic rocks and with vein filling. I. Kupriyanova (1977) divided the process of greisenization into three phases (Fig. 102): (1) early deposition (Al, K, Be, Li and F inflow, mica formation, predominance of feldspars in the veins); (2) acid leaching (Si inflow, leaching of all cations); (3) late deposition (Al, K, and Be inflow, predominance of quartz and muscovite in the veins). These three phases often represent the different vertical levels of greisen deposits succeeding one another upwards in the cited order. The mineral composition of greisens and beryllium mineralization depend on the composition

of the enclosing rocks involved in metasomatic processes. Accordingly, four different greisen ore formations can be distinguished (Table 1).

Apoultrabasic and apocarbonate greisens are of particular interest. The former occur as zones of phlogopite metasomatic rock (phlogopitite) usually 0.5 to 5 m in thickness including thin oligoclase, quartz-oligoclase and fluorite-oligoclase veins. The latter have a boudinage structure and occur as detached cores, lenses squeezed in phlogopitite glimmerite which, in its turn, is surrounded by actinolite metasomatic zone (Fig. 103). Oligoclase veins contain light green beryl, but glimmerite includes emerald, alexandrite and phenakite. Beryllium-bearing margarite and fuchsite are often developed at the margins of oligoclase veins. Such is the structure of typical emerald deposits which were regarded by A. Fersman as desilicified pegmatites.

Apocarbonate greisens are represented by fluorite metasomatites developed after limestones, which are pierced by numerous fissures filled with lithium margarite – aphesite, muscovite and phenakite which is replaced by chrysoberyl with depth.

The gradual transition into plutonogenic hydrothermal formations is characteristic of all greisen deposits.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

An association of bertrandite-phenakite-fluorite metasomatites which resembles apocarbonate greisens but is formed under

Table 1. Mineral Composition of Greisen Ore Formations

Ore formation	Host rocks	Principal ore minerals	Accompanying minerals
Apoalumosilicate	Sandstones, slates, granites, acidic volcanic rocks	Beryl, sometimes bertrandite developed after it	Zinnwaldite, muscovite, topaz
Apobasic	Amphibolites, actinolite-chlorite rocks	Beryl, phenakite, bavenite	Biotite, fluorite, epidote, calcite
Apoultrabasic	Peridotite, serpentinites, talc rocks	Emerald, chrysoberyl-alexandrite, phenakite	Phlogopite, fluorite, Be-margarite, oligoclase
Apocarbonate	Limestones	Phenakite, chrysoberyl, euclase	Fluorite, muscovite, ephesite
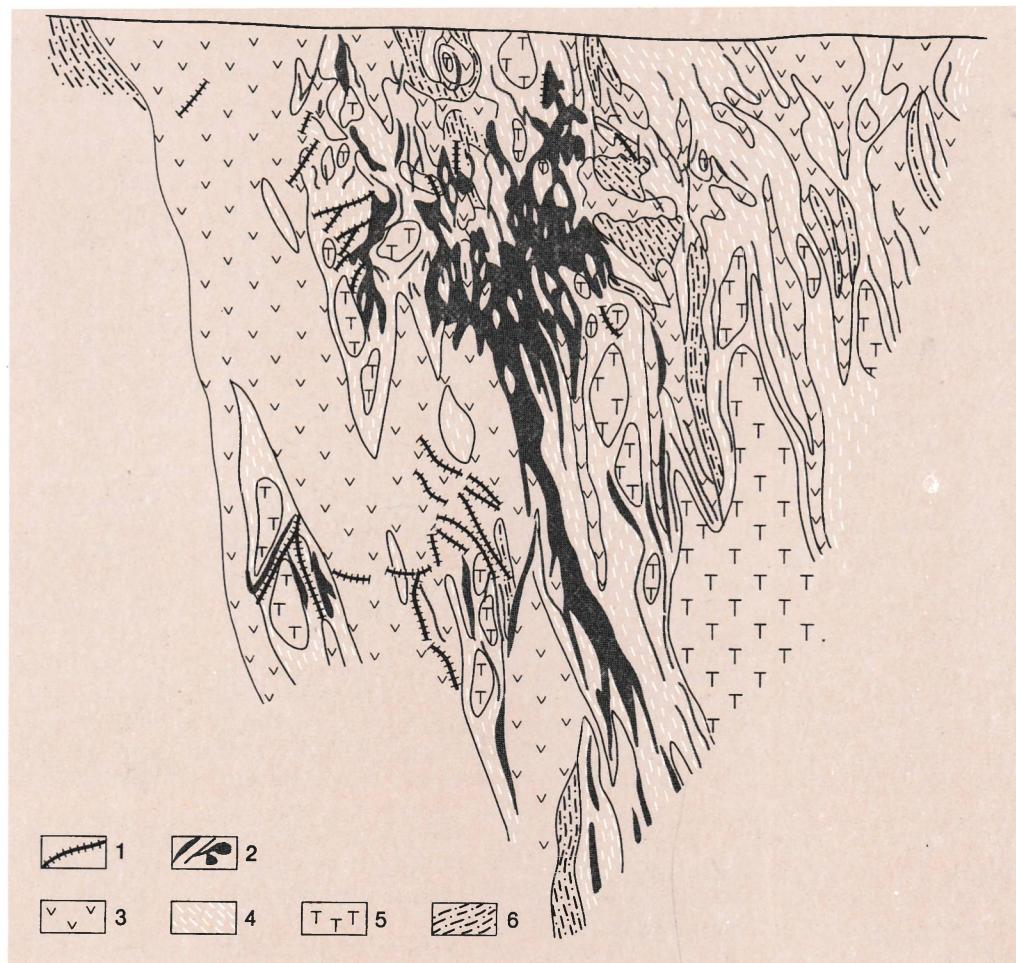
Fig. 103. Geological section of a beryllium deposit represented by phlogopite glimmerite–Apoultrabasic greisen:

1 – quartz-plagioclase veins;
2 – glimmerite ore-bearing zones;
3 – diorite and diorite porphyries;

4 – talc schists;
5 – serpentinites;
6 – silicic-carbonaceous shales and quartzites

somewhat different pressure and temperature conditions (Fig. 104) is attractive because of its high beryllium content (0.5-1.5% BeO). It is associated with small domes of hypabyssal albitized granosyenites, quartz syenites and alkaline granites confined to young zones of reactivation within consolidated fold areas. Where such domes are intruded in limestones and are accompanied by microsyenite and diorite-porphyry dykes, extensive fluoritization is developed above the domes and along the dykes. Fluoritization is preceded by skarn formation (vesuvian skarn) and microclinization. The ore bodies consist of massive and disseminated fluorite ores containing phenakite and bertrandite and more rarely leucophane and epididymite. A zonal structure of the mineralized bodies is readily recognizable.

Phenakite occasionally accompanied by thorite, rare earth minerals (ortite, bastnäsite) and pyrite occur in the immediate vicinity of subalkali granitoid domes; away from them, thorium and rare earth minerals disappear, bertrandite and calcite are present, the amount of sulfides
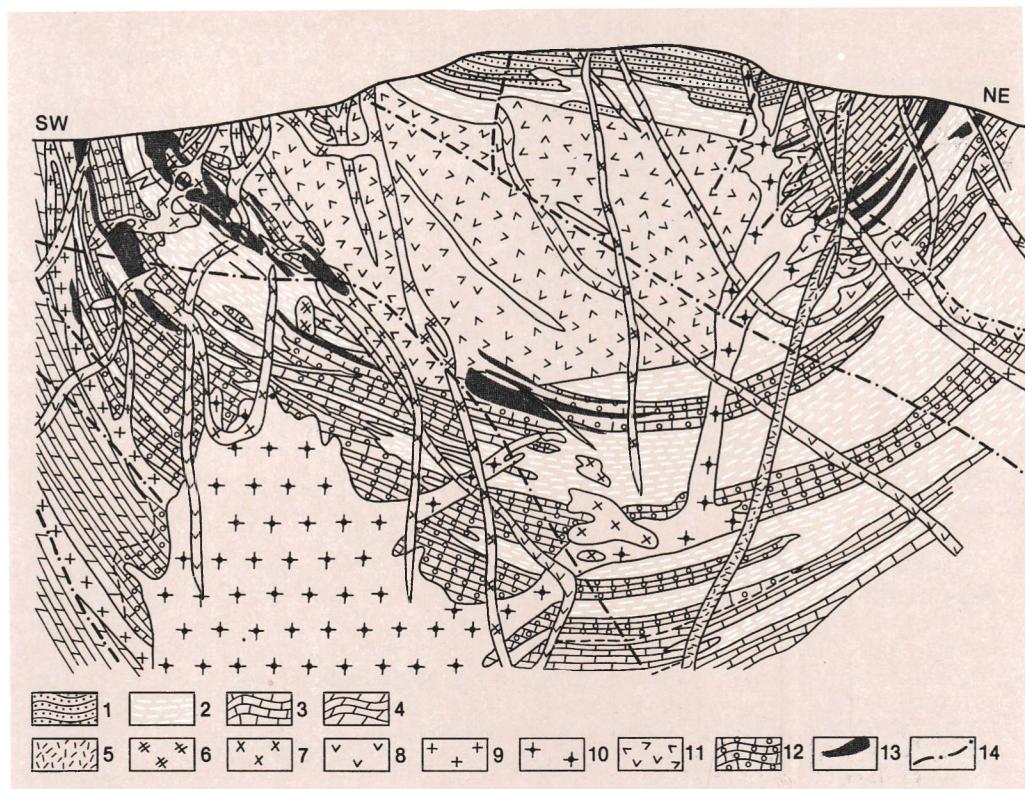
Fig. 104. Geological section of a bertrandite-phenakite-fluorite deposit. (After V. Galchenko):

1 – sandstone;
2 – shale;
3 – limestone;
4 – dolomite;
5 – felsite-porphyry;
6 – leucocratic syenite-porphyry;
7 – hornblende syenite-porphyry;

8 – diorite porphyrites;
9 – subalkalic granite and granosyenite;
10 – biotite granite;
11 – gabbro-diorite, granodiorite, and diorite;
12 – skarn;
13 – ore body;
14 – fault

increases, galena is widely developed, and barite and chalcedony appear. Ore localization is controlled by pre-mineralization dykes; rich massive ores occur where variously oriented dykes intersect or join one another. In the process of ore mineralization the dykes themselves were subject to fluoritization and beresitization. Apart from the dykes, ore may be localized in interbedded layers of limestones and aluminosilicate rocks, at the contacts of limestones and bed-like bodies of scapolitized gabbro-diorites; ore mineralization is never found in dolomite beds. An example of beryllium deposits of this type is the Ahuachili in Mexico and a number of deposits in the USSR.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

This type of beryllium-bearing deposits is commonly found at the margins of Tertiary depressions where they are associated with faults controlling the distribution of volcano-plutonogenic rock complexes. Ore occurs in sericitized and silicified, rhyolite tuffs and tuff lavas near rhyolite stocks and dykes. It is represented by scattered dissemination, thin veinlets and nodules – fillings of amygdule-shaped vugs. The principal beryllium minerals – bertrandite and its water-bearing varieties (helbertrandite, spherobertrandite) – are associated with chalcedony, opal, adular, fluorite, calcite, ankerite and hematite-specularite. The BeO

content in altered effusive rocks amounts to 0.5-0.7%. The largest deposit of this type is situated in the Utah State, USA.

The study of gas-liquid inclusions in beryllium and associated minerals is based on establishing the temperature ranges in which different deposits were formed. Pegmatitic and greisen deposits were formed in the range of 750 to 200 °C and the other types at 550 to 200 °C. It was found that beryl appeared at 740 to 130 °C, phenakite at 405 to 340 °C, genthelvite at 525 to 340 °C, bavenite at 300 to 250 °C, and bertrandite at 300 to 250 °C. The highest pressure determined by studying fluid inclusions in beryl from pegmatite was 3.5 kbar and in phenakite-fluorite metasomatites 0.6 to 0.7 kbar.

21 NIOBIUM AND TANTALUM DEPOSITS

Niobium and tantalum are two similar metals; they are intimately associated and found together. In 1801 the British chemist C. Hatchett was the first to isolate an oxide of a new element from a mineral found in Columbia; the new element was named columbium. In 1802 the Swedish chemist A. Ekeberg separated a similar oxide of another element which was named tantalum. Both elements had been regarded identical until in 1844 G. Rose proved that all tantalum-bearing minerals contain one more element similar to tantalum in its behaviour. He named it niobium. Hatchett's columbite proved to be a mixed mineral of niobium and tantalum. The name columbium had been used for niobium until the name niobium was officially adopted in 1950.

Both elements have high melting points. They are workable, malleable and resistant to high temperature and to the action of acids. Niobium is widely utilized in the form of ferrocolumbium as an alloying element in stainless steels. It is used in heat-resistant alloys applied in aerospace vehicles, supersonic aircraft and nuclear reactors. A small vertical capture section of thermal neutrons (1.1 barn) makes it perspective constructional material for nuclear reactors. With the addition of Sn, Zr and Ge niobium becomes a superconducting material at low

temperature (18 K). Tantalum is used in radioelectronics, in chemical engineering and in the production of superalloys.

The production of niobium (50-55% Nb_2O_5) and tantalum (60% Ta_2O_5) concentrates in the capitalist and developing countries was 35 000 tons and 1 000 tons, respectively (exclusive of the production of tantalum from tin smelter slags). Approximately 30 per cent of the total tantalum are produced as the by-product from tantalum-bearing tin smelter slags in Thailand, Malaysia and Zaire; thus, the total production of Ta_2O_5 in 1976 was 830 tons. In 1976 the price of pyrochlore concentrates (60% Nb_2O_5) was 2 440 US dollars per ton, columbite concentrates 3 366 US dollars and tantalite concentrates 26 000 US dollars.

The world resources (exclusive of the socialist countries) are 15 to 20 million tons of Nb_2O_5 and 0.2 to 0.3 million tons of Ta_2O_5. The unique niobium and tantalum deposits are the Borreiro de Araxá carbonatites in Brazil containing up to 4% Nb_2O_5 and the Bernic Lake pegmatites in Canada (0.24% Ta_2O_5). The deposits having the resources of more than 500 thousand tons of Nb_2O_5 and 10 to 15 tons of Ta_2O_5 are categorized as large ones and those with the reserves of less than 100 thousand tons of Nb_2O_5 and one to two thousand tons of Ta_2O_5 as small ones. High-grade deposits contain 0.4 to 0.5% Nb_2O_5 and 0.025% Ta_2O_5, and low-grade ones 0.1 to 0.15% Nb_2O_5 and 0.012 to 0.015% Ta_2O_5. Since tantalum is much more expensive and can be extracted as a by-product from niobium concentrates with a Nb/Ta ratio of not more than 20:1, all the deposits can be divided into niobium deposits (Nb/Ta > 20:1), tantalum-niobium (Nb/Ta between 20:1 and 5:1), and tantalum deposits (Nb/Ta between 5:1 and 1:3).

GEOCHEMISTRY AND MINERALOGY

Niobium in nature consists entirely of single isotope [93]Nb and tantalum of [180]Ta (0.012%) and [181]Ta (99.9%). Both elements are lithophile. Their highest concentrations

are related to granites (especially Ta), alkaline granites, nepheline-syenites, ultrabasic alkaline rocks, and carbonatites. Besides they are associated with the processes of alkali metasomatism. The crustal abundance of niobium is $2 \cdot 10^{-3}\%$ and that of tantalum is $2.5 \cdot 10^{-4}\%$. The average abundances of the elements in different rock types in $1 \cdot 10^{-4}\%$ are: 1 and 0.02 in ultrabasic, 20 and 0.48 in basic, 20 and 0.7 in intermediate, 20 and 3.5 in acid rocks, and 310 and 0.8 in nepheline syenites. The concentration factor is ~ 50 for both elements.

A rock-forming analogue of both elements is titanium. The substitution of Ti^{4+} by Nb^{5+} occurs in the following way: $Ti^{4+}Ca^{2+} \leftarrow \leftarrow Nb^{5+}Na^+$ or $2Ti^{4+} \leftarrow Nb^{5+}Fe^{3+}$. Where the Ti^{4+} concentration is high, Nb^{5+} and Ta^{5+} are dispersed in titanium-bearing minerals, and in the case of high Nb and Ta concentrations magmatic deposits with titanates enriched in niobium and tantalum (loparite, dysanalyte, perovskite) are formed.

Owing to a low coefficient of distribution of niobium and especially of tantalum between the products of fractional crystallization of palingenetic granite magmas and the residual liquid, both elements tend to concentrate in late-stage differentiates of multiphase intrusive complexes, the concentration of tantalum being more intense than that of niobium.

This explains why tantalum and niobium accumulate in granite pegmatites and in their shallow analogues – albitized rare-metal granites, and tantalum content increase in late phases and generations of tantaloniobates.

Due to high volatility of tantalum-fluorine complex compounds tantalum is partially extracted by fluorine and passes into a fluid, as is tin. In this process tantalum enters the composition of cassiterite in the form of microinclusions of tantalum minerals.

High concentrations of niobium and, to a lesser degree, of tantalum in carbonatites and in fault related feldspathic metasomatites are indicative of a deep-seated source of these elements.

In spite of the fact that tantalum and niobium have the same routes of migration and are always found together, the processes of their separation occur in nature. These processes are marked by a Nb/Ta ratio, the average ratio being $10:1$ to $12:1$. All the deposits of Ta and Nb in granites are characterized by a Nb/Ta ratio of $5:1$ to $1:3$. Geochemically, they are distinguished by high contents of F, Li, Rb, Cs, Be, Sn and sometimes W. The Nb/Ta ratio varies from $8:1$ up to $14:1$ in the deposits localized in subalkali and alkali granites and in zones of alkali metasomatism. In such deposits, niobium and tantalum are associated with F, Zr, TR_{Ce}, TR_Y, Th, U and more rarely with Li, Be, Sn and Mo. The deposits in miaskitic nepheline syenites are characterized by a Nb/Ta ratio of $50:1$ to $200:1$. In these deposits, Nb and Ta are associated with Zr, Th, TR_{Ce} and Ti. And finally, the deposits consisting of agpaitic rocks have a Nb/Ta ratio ranging between $12:1$ and $16:1$. F, Zr, Th, TR_{Ce} and Ti are typical for them. The deposits localized in carbonatites may contain both pure niobium ore with a Nb/Ta ratio of $100:1$ to $250:1$ and tantalum-niobium ore with the ratio varying within $2:1$ to $3:1$. Such deposits are distinguished by characteristic associations of Nb and Ta with Fe, Ti, Zr, P, TR_{Ce}, U, Th, Sr and Ba.

Over 50 minerals bearing Nb and Ta are known exclusive of numerous varieties. The most important ore minerals are a columbite-tantalite group (Fe, Mn) (Nb, $Ta)_2O_6$ (75-86% Nb_2O_5 + Ta_2O_5), wodginite (Mn, Fe) (Ta, $Sn)_2O_6$ (70% Ta_2O_5), a pyrochlore-microlite group (Ca, $Na)_2$ (Nb, $Ta)_2O_6$(OH, F) (30-70% Nb_2O_5 + $+Ta_2O_5$) including numerous varieties (uranium- and tantalum-bearing pyrochlore-hatchettolite, rare-earth- and tantalum-bearing pyrochlore-marignacite, plumbopyrochlore and others), loparite (TR_{Ce}, Na, Ca)(Ti, Nb, Ta)O_3 (8-20% Nb_2O_5 + Ta_2O_5), fergusonite $YNbO_4$ – brochanite $CeNbO_4$ – (38-58% Nb_2O_5), and others. The columbite group minerals, fergusonite and loparite are extremely resistant to weathering and may accumulate essentially in placer deposits.

METALLOGENY

Niobium and tantalum deposits are formed in relation to granite magmatism during an intermediate and a late phase of a geosynclinal cycle. They appear in the periods of platform reactivation being associated with alkali intrusions and deep originated alkali solutions. Tantalum-bearing pegmatites are known to be of all ages but the largest and richest deposits are usually of Lower or Middle Proterozoic age (Bernic Lake in Canada, Bikita in Zimbabwe, Wodgina in Australia). The deposits represented by fault-related feldspathic metasomatites occur in zones of reactivation of ancient stabilized fold structures; they are commonly of Upper Proterozoic age. Carbonatites confined to deep-seated faults within platform regions are not older than 1 800 million years; most often they are Phanerozoic in age. The youngest deposits are confined to domes of albitized rare-metal-bearing granites formed during the late stage of development of geosyncline-fold areas; they are commonly Mesozoic in age.

TYPES OF COMMERCIAL DEPOSITS

The commercial types of niobium and tantalum deposits are: (1) magmatic; (2) pegmatitic; (3) albitite; (4) feldspathic metasomatites; (5) carbonatite; (6) weathering; and (7) placers.

MAGMATIC DEPOSITS

This type of deposits includes loparite-bearing stratified massifs of agpaitic nepheline syenites related to tectono-magmatic reactivation of ancient shields and represented by central-type massifs circular in plan and funnel-shaped in vertical section. One such massif having a multiphase structure is known to be 300 km^2 in area (Fig. 105). It consists of three successively formed rock complexes: poikilitic nepheline syenites, stratified rocks of a lujavrite-foyaite-urtite series, and eudialyte lujavrites intruding and partially overlying them. Mineralization is localized in the stratified complex. It consists of rhythmically alternating, very persistent and flat-lying
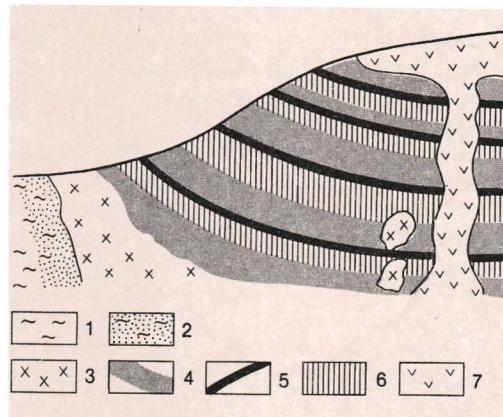
Fig. 105. Schematic geological section across a massif of stratified nepheline syenites:

1 – Archean gneiss;
2 – fenite;
3 – poikilitic and porphyritic nepheline syenites;
4-6 – stratified complex:
4 – foyaite;
5 – loparite lujavrite;
6 – urtite;
7 – eudialite lujavrite

layers of leucocratic (urtite, juvite), mesocratic (foyaite) and melanocratic (lujavrite, malignite) alkali rocks which are regularly interstratified to form repeated cycles. The amount of dark coloured constituents (alkali pyroxenes and amphiboles) and accessory minerals, e.g. loparite, increases from the upper layers to the lower ones within each cycle. Loparite concentrates in the lower levels of the most melanocratic layers of the cycles in the rocks of lujavrite and malignite composition where its content amounts to 5-10%. As a result, unusual ore bodies represented by thin "beds" appear ranging between 0.4 or 0.5 and 1 or 2 m in thickness and extending throughout the massif. The mineral assemblage consists of nepheline, sodium-potassium feldspar, aegirine, alkali amphibole, sodalite, zeolite, and accessory minerals such as loparite, villiaumite, apatite, eudialyte, ramsayite, murmanite-lomonosovite, sphene, magnetite, pyrite and pyrrhotite.

Loparite is a complex ore from which Ta, Nb, TR$_{Ce}$ and Ti are extracted. Loparite mineral concentrates contain 0.5-0.6% Ta$_2$O$_5$ with a Nb$_2$O$_5$/Ta$_2$O$_5$ ratio of 13:1 or 14:1.

PEGMATITIC DEPOSITS

Tantalum is extracted as a by-product from spodumene pegmatites (see "Lithium Deposits") and from pegmatites containing pollucite (see "Cesium and Rubidium Deposits"). The bulk of the world production, however, is derived from microcline-spodumene-(petalite)-albite pegmatites containing 0.02-0.03% Ta_2O_5 with a Nb/Ta ratio of 1:1 to 1:3.

Tantalum mineralization is represented by columbite-tantalite, ixiolite and manganotantalite of different generations and varieties. Along with large segregations, fine dissemination is always present. In the case of a high concentration of tantalum and a low content of iron, wodginite appears instead of manganotantalite and cassiterite. Microlite and sometimes simpsonite, ugandite, stibiotantalite and other tantalum minerals are formed at the late stage of mineralization in the course of lepidolitization. Tantalum mineralization becomes less intense with depth, and lithium concentration increases. Geochemically, pegmatites are characterized by high values of Mn, Ta > Nb, Li, Rb, Cs, Be, B, Sn, P, Tl and Ga and by occasional appearance of Bi and Sb. Along with dike series, in some regions of the world (the Black Hills of South Dakota, USA, and the Mongolian Altai, China) occur compositionally similar pegmatites represented by zoned, fully differentiated stocks and pipes. In such deposits, mineralization is of the pocket type, and ore minerals in pockets may be gigantic in size (Etta Mine, Black Hills).

ALBITITE DEPOSITS

Deposits of this type were formed in fold areas during the post-orogenic stage of their development and are associated with multiphase granite complexes. Granites of the late phase are localized at the intersections of tectonic zones and occur in the form of small stocks or domes less than one km² in size formed at depths of 1 to 2.5 km. The tops of the domes are often complicated by protrusions and apophyses. In some places these grade into dykes which may have a subeffusive appearance and contain glass of topaz composition (ongonite).

The composition of such stocks is unusual; they contain microcline and "pea-shaped" quartz grains growing in a fine- to medium-grained granite mass. At the same time they are enriched in albite and contain topaz (up to 20%), zinnwaldite or lepidolite, cassiterite, columbite-tantalite, microlite, struverite, wolframite and sphalerite (Fig. 106). Microcline is often amazonitized, and numerous veins and veinlets of quartz-amazonite composition are observed in the granite. Where such domes
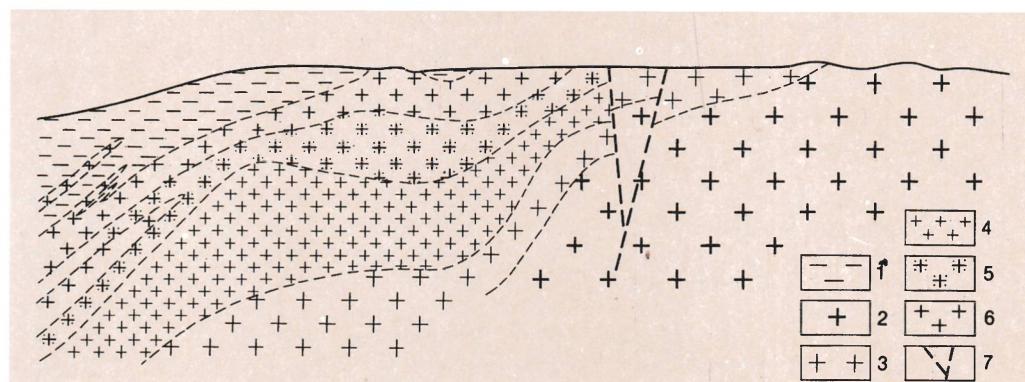
Fig. 106. Geological section across rare-earth-bearing albitites. (After N. Zalashkova):

1 – shale and sandstone;
2 – porphyritic two-mica granite;
3 – porphyritic albite-microcline granite with muscovite;
4 – amazonite-albite granite with zinnwaldite;
5 – tantalum-bearing amazonite-albite granite with zinnwaldite and lepidolite;
6 – albite granite with lepidolite and highest tantalum concentration;
7 – fault

intrude sandstone and shale sequences, zinnwaldite greisens are developed above them and on the sides of their gently dipping contacts, and where they occur in limestones, fluoritized zones are formed which often carry beryllium mineralization. With depth tantalum mineralization disappears, lepidolite is replaced by zinnwaldite and farther downwards by protolithionite, the content of cassiterite and topaz reduces, the amount of albite decreases, and the rock grades into a poorly albitized protolithionite granite. Quartz veins carrying tin-tungsten mineralization are commonly found above albitite domes.

The Ta_2O_5 content in the apical parts of the domes is 0.01-0.02%. It is 0.03-0.04% immediately below the cover of the dome rapidly decreasing with depth.

A peculiar variety is represented by nepheline syenite albitite. Massifs of miaskitic nepheline syenites are often intensely albitized along the contacts so that both nepheline syenites and the host metasedimentary rocks are transformed to albitite. The process is commonly controlled by tectonic zones running along the contacts of alkali rock massifs. Carbonatization may locally occur instead of albitization. Both processes are productive in relation to rare-metal mineralization, albitization produces pyrochlore and zircon, carbonatization introduces pyrochlore. Mineralization is usually of low commercial value because of low Nb_2O_5 and ZrO_2 contents.

Apart from the described tantalum-bearing albitites, zones of reactivation of stabilized fold structures include minor massifs of subalkaline and alkaline granites bearing Zr, Ta-Nb, Th and cryolite. These granites can be classified as a separate formation of rare-metal subalkaline granites. In mineral composition and other properties they are similar to fault-related feldspathic metasomatites.

DEPOSITS OF FELDSPATHIC METASOMATITES

Niobium and tantalum deposits of this type are localized in zones of tectonic reactivation and are associated with regional faults running either in the basement of platforms or in areas of completed folding. The processes of alkaline metasomatism occur along the faults and affect progressively metamorphosed rocks of different composition. They are most intense at the intersections of faults, flexure-like bends, periclinal closures of folds, etc. Intense feldspathization, albitization and silicification produce quartz-feldspathic rocks which resemble syenites, quartz syenites and alkali granites. Where gneisses are involved into the process, biotite is replaced by riebeckite-arfvedsonite and later by aegirine. Metasomatic activity has never been noted to be associated with surrounding intrusive rocks.

Metasomatites often contain up to 5-10% of cryolite (with various alumofluorides developed after it), fluorite, fluocerite, gagarinite, zircon and malacon, tantalum- and rare-earth-bearing pyrochlore (marignacite), plumbopyrochlore, and more rarely columbite, fergusonite, ilmenite and thorite. The deposits are represented by disseminated and stringer-disseminated ore accumulations of an elongate form having no distinct geologic boundaries. The principal ore mineral is pyrochlore enriched in TR and containing 4-6% Ta_2O_5 with a Nb/Ta ratio of 10:1 to 12:1. The deposits contain 0.15-0.2 to 0.6% Nb_2O_5 and 1-2% ZrO_2. Geochemically, they are distinguished by high percentages of F, Zr, Nb > Ta, TR_{Ce}, TR_Y, Th, U, Mo and occasionally Li, Sn and Be.

CARBONATITE DEPOSITS

Carbonatites and their weathering crusts have become important sources of niobium. All carbonatite deposits occur within the stable parts of the continents such as platforms and ancient schields, being closely related to deep-seated faults. Carbonatites can be subdivided into two groups.

(1) Rounded and more rarely lens-like central-type concentric massifs in which carbonatites appear as the final differentiates of ultrabasic-alkaline rock complexes. Within such zoned massifs, ultrabasic rocks (olivinite-peridotite) are seen to be succeeded inwards by later nepheline-pyroxene rocks and less frequently by jacupirangite-meltei-
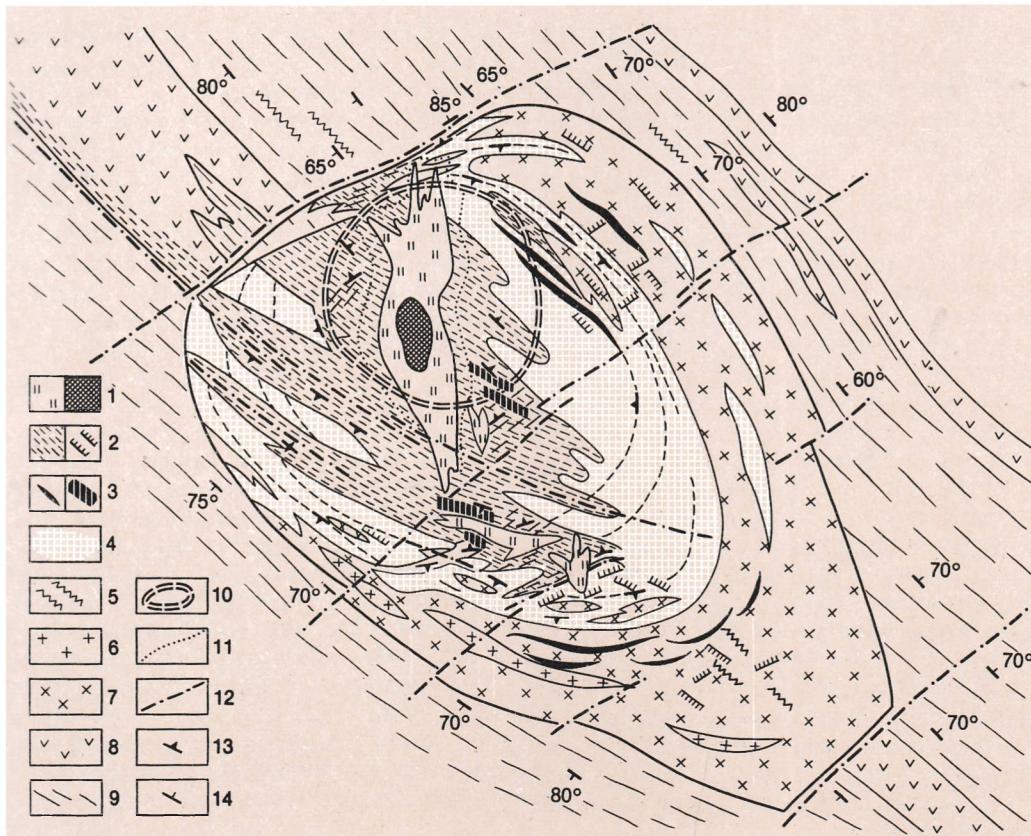
Fig. 107. Structure of the Lower Sayan zoned massif of ultrabasic-alkalic rocks and carbonatites. (After A. Frolov):

1 – ankerite carbonatites (a – fine-grained; b – coarse-grained);
2 – amphibole-calcite carbonatites (a – zones; b – veins);
3 – pegmatoid forsterite -and diopside-calcite carbonatites (a – vein-shaped bodies; b – remnants and relicts in later formations);
4 – coarse-grained augite-biotite-calcite carbonatite;
5 – picritic porphyry-alnoite;
6 – alkaline and nepheline syenites;
7 – jacupirangite-ijolite-urtite rocks;
8 – gabbro-diabase;
9 – quartz-micaseous schist and sandstone;
10 – outlines of picritic porphyry-alnoite relicts;
11 – halo of ankeritized calcite carbonatite;
12 – fault;
13 – banding in carbonatite;
14 – dip and strike of schistosity and bedding

gite-ijolite, melilite rocks, nepheline syenites and carbonatites which occur in the centres of such concentrically zoned massifs (direct zoning). Less frequently an inverse picture can be observed where carbonatites encircle the rounded massifs as ring dykes, the centres of the massifs being composed of ultrabasic rocks (inverse zoning).

Massifs of carbonatites and ultrabasic-alkaline rocks may be formed at various depths, including those produced by volcanic activity at the earth's surface, e.g. actual carbonatite lavas at Oldoinyo Lengai in Tanzania, and ancient volcanic cones whose vents are filled with carbonatites. These massifs, however, are devoid of rare-metal mineralization. Deeper massifs are characterized by a greater extent of carbonatites usually ranging between 0.1-0.2 and 2-3 km^2 and sometimes reaching 20 km^2 in area. They always contain disseminated apatite, pyrochlore, baddeleyite and phlogopite. Such massifs occur in the East Sayan (Fig. 107), Aldan and Jugjur in the USSR, and in Canada (Oka, St. Honoré).

Carbonatites are often accompanied by peculiar apatite-forsterite-magnetite rocks with calcite which are referred to in

literature as phoscorites, camaforites and nelsonites. In some cases the rocks are extremely abundant in magnetite and grade into iron ores, e. g. in the Kovdor massif, USSR, and in others apatite prevails greatly over the other constituents, e. g. in Palabor, South African Republic, but in all the cases they contain baddeleyite, hatchettolite, pyrochlore, zirkelite and chalcopyrite. The carbonatites themselves are multiphase formations; the early calcitic carbonatites are replaced by dolomitic ones and later by ankeritic varieties which terminate the carbonatite process. Pyrochlore and hatchettolite mineralization accompanied by apatite, baddeleyite and zirkelite occurs chiefly at the end of the calcitic stage. In the process of ankeritization, pyrochlore is pseudomorphously replaced by columbite. Some zones and patches in carbonatite containing more than 0.3-0.7% Nb_2O_5 are developed on the general background of low values of Nb_2O_5 (0.1-0.15%). For instance, the average content of Nb_2O_5 in the Niobec (St. Honoré, Canada) ore is 0.6-0.7%.

There is no change in mineralization to a depth of 1 to 1.5 km.

(2) Linear carbonatite zones are often developed in ancient rock sequences, exhibiting no association with ultrabasic-alkaline rocks but accompanied by broadly manifested fenitization of the enclosing rocks (most commonly gneisses). Instead of pyrochlore, the principal ore mineral is brochanite – a cerium-bearing analogue of fergusonite (the Ukrainian crystalline schield, USSR).

DEPOSITS OF WEATHERING

Recent areal crusts of weathering enriched in columbite are found in tropical countries where columbite-bearing granites are widely developed. Such are the young alkaline granites of the Jos Plateau in Nigeria which were emplaced in ring faults during a Mesozoic reactivation of the Nigerian crystalline basement. Apart from the crusts of weathering, high concentrations of columbite are found in diluvial-alluvial placers at the hill slopes and in alluvial placers in the valleys of rivers flowing from the plateau. Approximately 65% of columbite are produced from the weathered granites and 35% from the placers.

Of significant value are areal and especially linear crusts of weathering over carbonatites, containing up to 10-15% P_2O_5 and 1-4% Nb_2O_5. Linear crusts of weathering confined to fault zones, often extend to a depth reaching 100 m. In some massifs, linear crusts consisting of limonitized fine-grained sand which grades with depth to desintegrated ochreous carbonatite are overlain by alluvium and karstified.

PLACER DEPOSITS

Diluvial-alluvial and alluvial tantalite placers are known to have been formed as a result of the erosion of rare-metal-bearing pegmatite fields. Such placers are regarded as commercially important with the lowest tantalite content of 10-15 g/m³. A large number of flat-lying tantalite-bearing pegmatite bodies, and the action of erosion on the pegmatites throughout their extent which is possible where river valleys follow the strikes of the pegmatite fields are especially favourable for the formation of placers. Because of tantalite friability it is usually not transported for a distance of more than one kilometre from the place where it is released from its enclosing rock by weathering. So, it accumulates essentially in or near the source area usually together with cassiterite. Concentrates derived from such placers always consist of tantalite and cassiterite with the latter prevailing over tantalite. Under the conditions of intense tropical weathering, the availability of extensive pegmatite fields and a favourable geomorphological situation, a great number of small placers were formed with the Ta_2O_5 reserves ranging within a few dozens to a few hundred tons each. Such placers are mined in Zaire, Nigeria and Brazil.

Loparite is also a stable mineral. Being released from its enclosing rock it accumulates in lake beds near the massifs of loparite-bearing agpaitic nepheline syenites and in fluvioglacial formations produced by the erosion of moraines carrying boulders of loparite-bearing rocks. Fluvioglacial placers are of low economic value because of the high stone content.

22 ZIRCONIUM AND HAFNIUM DEPOSITS

Zirconium and hafnium have strong geochemical similarity and are always found together in rocks and minerals in which they occur.

Zirconium was isolated as an oxide from zircon by the German chemist M. Klaproth in 1789 and was named after this mineral. The existence of hafnium was predicted by D. Mendeleyev, and the element was discovered by the Danish scientists G. Hevesey and D. Coster in 1923.

The high melting point, resistance to acids and melts, a low neutron absorption cross section (0.18 barn) and the other properties of zirconium determine its applications. It is a perfect material for containers of nuclear fuel elements and for structural materials in nuclear reactors. It is used as an additive in non-ferrous alloys applied in aircraft and automobile industry. Because of its refractory nature zircon is used as mold material for casting ferrous metals in foundries and in bricks and blocks in glass furnaces. Hafnium, having a melting point of $3900\,°C$, is used in the form of carbide to produce heat-resistant articles.

In 1976 the production of zirconium concentrates containing 66% ZrO_2 was 500 000 tons in the capitalist and developing countries. Approximately 75% of the world production are accounted for by Australia and the USA (Florida). Hafnium if extracted only as a by-product in the processing of zirconium concentrates. Its production does not exceed 30 to 40 tons per year. The price of one ton of zirconium concentrates in 1977 was 115 to 560 US dollars, one kilogram of zirconium sponge 15.4 US dollars, and one kilogram of hafnium 100 to 270 US dollars (depending on the grade). Practically, all the world production of zirconium concentrates is derived from sea-beach placers in which zircon occurs together with ilmenite, monazite and rutile. In many countries, e. g. in India and others, zircon is produced as a by-product from ilmenite and monazite placers. The placers are categorized as large ones if they contain more than 200-300 million cubic metres of productive sands, as small ones if the reserves are 30 to 70 million cubic metres, as high-grade ones if the zircon content is higher than 30-35 kg/m^3, and as low-grade ones with less than 20 kg/m^3 of zircon with a ratio of by-product ilmenite to zircon being 3 to 1.

GEOCHEMISTRY AND MINERALOGY

Zirconium is a lithophile element forming ZrO_2 and numerous silicates; hafnium acts as an isomorphous substitute of zirconium being its absolute geochemical analogue. Zirconium has stable isotopes ^{90}Zr (51.46%), ^{91}Zr (11.23%), ^{92}Zr (17.11%), ^{94}Zr (17.40%), and ^{96}Zr (2.8%). The stable isotopes of hafnium are ^{174}Hf (0.18%), ^{176}Hf (5.20%), ^{177}Hf (18.50%), ^{178}Hf (27.14%), ^{179}Hf (13.75%), and ^{180}Hf (35.24%). The crustal abundance of zirconium is $17 \cdot 10^{-2}$ and hafnium $3 \cdot 10^{-4}\%$. The average abundance of Zr and Hf in different rock types, in $1 \cdot 10^{-4}\%$, are: 30 and 0.1 in ultrabasic, 100 and 1 in basic, 200 and 1 in acidic, and 680 in nepheline-syenitic rocks.

Zirconium has a tendency to concentrate in alkaline rocks, its content in them being two times as high as in granites.

Since zirconium has no direct geochemical analogues among the rock-forming elements, it forms its own accessory minerals during a magmatic stage and practically does not participate in post-magmatic ore formation associated with granitic magmas. It is only where alkaline magmatism is developed that zirconium concentrates during high-temperature post-magmatic processes (in association with development of albitization), which is explained by its high migration capacity in alkaline solutions.

Different types of minerals which contain zirconium vary depending on the ratio $(K_2O + Na_2O):Al_2O_3$ in melts and solutions, i. e. with an agpaitic coefficient, and on the amount of SiO_2. Zircon is formed in plumasitic rocks $(K_2O + Na_2O < Al_2O_3)$, eudialyte in agpaitic rocks $(K_2O + Na_2O > Al_2O_3)$, and lavenite, wöhlerite and other zirconium silicates are formed at $K_2O + Na_2O = 1$. Baddeleyite is formed under the conditions of low SiO_2 activity (in carbonatites).

Hafnium always follows zirconium but the

ratio Zr/Hf varies with alkalinity–acidity of a mineral-forming environment and a kinetic factor. In fractional crystallization, hafnium lags behind zirconium and concentrates in the latest residual products. Its highest concentrations (up to 10-15% HfO_2) are observed in late-phase zircons (malacon, alvite) associated with the processes of alkaline metasomatism.

Zircon is extremely resistant to weathering under exogenous conditions; it accumulates in placers and in fine fragments occurs in sandy-clayey rocks.

Approximately 30 minerals of zirconium are known but only two minerals, zircon $Zr(SiO_4)$ (65% ZrO_2) and beddeleyite ZrO_2 are of commercial value.

TYPES OF COMMERCIAL DEPOSITS

In endogenous deposits, zircon concentrates are obtained as by-products in the recovery of columbite or pyrochlore ores of alkaline granites and feldspathic metasomatites containing 1-2% ZrO_2. Zircon of these deposits is enriched in hafnium (Zr/Hf = 15). Besides, zircon is extracted as a by-product in mining of pyrochlore-bearing albitites associated with nepheline syenites. Baddeleyite began to play an important part in industry when the commercial utilization of carbonatites began. Baddeleyite concentrates are obtained as by-products in combined mining of forsterite-apatite-magnetite ores and pyrochlore carbonatites occurring in massifs of ultrabasic-alkaline rocks. Examples are the Kovdor deposit in the Kola Peninsula, USSR, and the Palabor deposit, South African Republic.

Strictly zirconium deposits are found only in recent and fossil sea-beach placers widely developed in Australia, the USA, India, Brazil, Sri Lanka, South Korea and China. Examples of recent placers are those of the eastern coast of Australia which supply approximately 50% of the zirconium concentrates produced in the world.

AUSTRALIA EASTERN COAST. Placers extend along the sea coast in a meridional direction for a distance of 1 100 km from the Fraser Island to the Jervis Bay. The placers are located within narrow strips of sand–beaches–ranging within 10 to 70 m in width. Many of the beaches extend along a curved coast between two sand bars in tide-flooded bays. The bedrock source of the material supplied to the placers is the weathering crust of granites and products of their erosion, which compose the Great Dividing Range extending parallel to the shoreline. As a result of the disintegration of granite weathering crusts, accessory minerals accumulated in the Jurassic sands of the Morton district, which served as intermediate collectors of heavy minerals. The richest placers are found in the estuaries of the rivers flowing into the ocean and on the shores open to the surf.

The content of heavy minerals–a heavy concentrate–in a sea-beach zone varies within 5 to 9%. A heavy concentrate contains up to 50% zircon and 5 to 50% rutile and ilmenite. Besides, magnetite, monazite, tourmaline, topaz and occasionally cassiterite are present. As a result of heavy storms the partial regeneration of beach placers depleted by mining takes place. Along with the beach placers and in the immediate vicinity beyond them occur heavy mineral-bearing foredunes formed of the sand transported and sorted out by the wind. Some dunes are as high as 15 m; they may extend for distances of a few kilometres. Buried ore-bearing dunes have been discovered. In some of the placers, the reserves were estimated at 3.2 to 3.5 million tons of zircon, 4.2 million tons of rutile and 3.2 million tons of ilmenite.

23 DEPOSITS OF RARE-EARTH METALS AND YTTRIUM

The rare-earth group of metals also known as lanthanides comprises 15 geochemically similar elements having atomic numbers 57 through 71 and occupying the same position in the Mendeleyev's periodic system. The term "rare earth" was derived from the latin "terra rarae" and abbreviated accordingly as TR. The other group symbol, Ln, was derived from "lanthanides". The group includes lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), pro-

metium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Only one of these, Pm, has been artificially produced. Yttrium (Y) is one more element generally classed with the rare-earth metals because of its chemical similarities and geochemical affinities, though it is not a formal member of the group and occupies its own position in the periodic system.

The rare-earth group is usually divided into two subgroups: the cerium subgroup (La-Ce-Pr-Nd-Sm-Eu-Gd) designated as TR_{Ce}, and the yttrium subgroup (Tb-Dy-Ho-Er-Tu-Yb-Lu) designated as TR_Y, although yttrium is usually not included into this subgroup. For geochemical purposes, it is convenient to divide the rare earth group into three subgroups (D. Mineyev, 1969, 1974): the lanthanum Σ(La-Nd), yttrium Σ(Sm-Ho), and scandium Σ(Er-Lu) subgroups. Compositions of the rare earth group, accordingly, can be represented by means of a triangular diagram having the coordinates: Σ(La-Nd) $-\Sigma$(Sm-Ho) $-\Sigma$(Er-Lu).

The history of the discovery of rare earths can be traced as far back as 1794 when the Finnish scientist I. Gadolin analyzing the mineral ytterbite (named later gadolinite) from a quarry near the town of Ytterby found that the mineral contained a "new earth" which was named an "yttrium earth". In 1803 J. Berzelius and V. Hizinger discovered a "cerium earth". The same discovery was made independently by M. Klaproth. For a long time these elements were regarded as rare ones and were believed to be of little practical value. They began to be utilized only in the early 20th century in gas mantles for gas-lamps. In the midthirties, the discovery of their alloying action on steel, cast iron, and nonferrous metal alloys has contributed greatly to the expansion of the rare-earth industry. Many new applications of rare earths discovered in the past 25 years increased their usage. Applications are in special alloys, special types of glasses, as petroleum-cracking catalysts, in phosphors for colour-television tubes and high-intensity lighting, in supermagnetic alloys of Sm with Co, in lasers, and in synthetic rare-earth garnets – masers – for microwave amplification. Isotopes ^{170}Tu, ^{155}Eu, and ^{144}Ce are used as radiation sources, control rods of Gd, Sm and Eu are applied in nuclear reactors, etc. Rare earths. are presently used by the industry both as various mixtures (e. g. misch metal), and as individual elements. Of great significance in the latter applications are Ce, La, Nd, Sm, Gd, and especially Eu, Y, and Tu. The most important consumers of rare earths are petroleum industry, metallurgy, and ceramics.

The production of rare-earth concentrates (with 60% TR_2O_3) in the capitalist and developing countries was reported to be 50000 tons with 66% of this total produced in the USA. In 1976 the price of one ton of bastnaesite concentrate was 660 US dollars and one ton of monazite concentrate 225 US dollars.

For the last 20 years, a great change was observed in the rare-earth source materials. Previously, all the elements of the cerium subgroup were extracted from thorium containing monazite ores of sea-beach placers. Presently, the extremely low demand for thorium resulted in switching of the rare-earth industry chiefly to processing of bastnaesite concentrates from the Mountain Pass deposit, California, USA. Significant amounts of rare earths (about 35%) are obtained as by-products from the processing of tantalum-niobium (loparite, fergusonite) and uranium (brannerite, phosphate) ores. The deposits are classified as large ones if they contain more than 400-500 thousand tons of TR_2O_3, and as small ones – less than 100 thousand tons; high-grade ores contain more than 1-2% TR_2O_3, and low-grade ones – less than 0.3-0.4%.

GEOCHEMISTRY
AND MINERALOGY

The rare-earth metals and yttrium are lithophile elements whose concentrations are related to granite and alkaline magmatism. The TR_{Ce} elements accumulate in all the types of alkaline rocks, the highest values being found in the alkaline rocks of obvious mantle origin, whereas the TR_Y elements concentrate where granite and alkali-granite magmatism is developed (Table 2).

Table 2. Abundances of Rare Earths in Different Rock Types, in $1 \cdot 10^{-4}$%
(Data from Y. Balashov, 1976)

Rock type	TR	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
Crust	112	23	16	31	4.5	17	4.2	1.3	4.2	0.7	3.8	0.9	2.6	0.4	2.3	0.3
Tholeiite (oceanic)	82	32	33	10.3	1.9	9.9	3.5	1.3	5.0	0.9	5.2	1.2	3.5	0.5	3.2	0.5
Basalt (continental)	189	27.3	32	59	7.8	40	6.6	1.9	6.2	1.0	—	1.0	2.9	0.4	2.6	0.4
Granite	288	42	50	100	11.4	46	8.3	1.1	7.6	1.1	—	1.6	4.7	0.7	4.8	0.8

The concentration factor is 50 for TR, and 100-150 for Y.

The principal geochemical features of the rare-earth metals and yttrium are as follows. The petrogenic analogue of the rare-earth elements and Y is Ca^{2+} which is easily substituted isomorphously by TR^{3+} in the following way: $2Ca^{2+} \leftarrow Na^{+}TR^{3+}$, $Ca^{2+}Nb^{5+} \leftarrow TR^{3+}Ti^{4+}$, $Ca^{2+}Si^{4+} \leftarrow TR^{3+}Al^{3+}$. The formation of rare-earth minerals is possible in the rocks having the ratio $100 \, TR_2O_3/Ca > 1$; at lower values of the ratio the rare-earth elements disperse in rock-forming minerals. Amphiboles and pyroxenes are commonly enriched in the light rare-earth elements and feldspars in the heavy ones.

The rare-earth elements of intrusive rocks increase from ultrabasic rocks, through acidic, to alkaline rocks. The highest concentrations are related to agpaitic alkaline rocks and to the latest products of gabbroid-alkaline and ultrabasic-alkaline magmas.

In association with granite magmatism, the rare-earth elements concentrate during the magmatic stage, entering the composition of accessory minerals (monazite, xenotime, orthite), and in residual formations – pegmatites – especially in deep-seated ones. The role of rare earths is negligible in hydrothermal activity. Where alkali and especially alkali-granite magmatism is developed, the rare-earth elements accumulate in post-magmatic formations.

Rare earths are fluophile elements and are extractable in the form of alkali-fluoride, alkali-fluohydroxyl and alkali-carbonate complexes. They are distinguished by high geochemical affinities with F^{-}, $[CO_3]^{2-}$, $[PO_4]^{3-}$, and $[SO_4]^{2-}$ and form with them stable complexes easily soluble in a broad temperature range, the complexes formed with Y and TR_Y being more stable than those with TR_{Ce}. For this reason TR_Y are transported for greater distances than TR_{Ce}, especially in metasomatic activity.

Because the ionic radii of the rare-earth elements are similar to those of uranium and thorium, they enter the composition of many uranium and thorium minerals from which they can be extracted as by-products, the TR_Y exhibiting a more intimate geochemical affinity with U and TR_{Ce} with Th.

Despite the fact that the rare-earth elements have the similar geochemical properties and are always found together they may be fractionated in the course of different mineral-forming processes. The principal mechanisms of a natural fractionation of the rare-earth elements are (V. Shcherbina, 1959; Yu. Balashov, 1976):

(1) crystallochemical mechanism based on the fact that the ionic radii of the rare-earth elements decrease progressively from La (1.14 Å) to Lu (0.85 Å). Therefore TR_Y^{3+} are more intimately associated with Sc^{3+} (0.81 Å), Mn^{2+} (0.80 Å), and Zr^{4+} (0.79 Å), in whose minerals they may concentrate, while TR_{Ce}^{3+} are geochemically related to Sr^{2+} (1.12 Å), Ba^{2+} (1.34 Å), and Th^{4+} (1.02 Å). The petrogenic analogue of the rare-earth elements, Ca^{2+} (0.99 Å), is equally related to TR_Y^{3+} and TR_{Ce}^{3+}. As a result, minerals with the "complex" TR compositions, in which the rare-earth elements substitute Ca^{2+}, or with the "selective" ones in which the rare-earth elements substitute Mn^{2+}, Zr^{4+}, Sc^{3+} or Sr^{2+} and Ba^{2+}, are formed;

(2) basicity differences of the rare-earth elements whose ionic potentials increase from La to Lu leading to a decrease in basicity which is, after Jost relative units, La$-2\,500$, Nd-100, Sm-20, Gd-7, and Dy-1. Consequently, the TR_{Ce} elements concentrate in ultrabasic-alkaline magmas whose basicity is very high, and TR_Y and Y in alkali-granite ones;

(3) different ability to form complexes and stability of complex compounds. Carbonate complexes with TR_Y are more stable than with TR_{Ce}, which explains a late precipitation of minerals with TR_Y and their more durable migration. The same behaviour is observed in complexes with K and Na: TR_Y accumulate in relation to potassium metasomatism, and TR_{Ce} in relation to sodium;

(4) oxidation-reduction potential which controls the separation of the rare-earth elements in oxidation-reduction reactions. For instance, in the alkali environment, Ce^{3+} is easily oxidized to Ce^{4+} and is separated from the other rare-earth elements. In the acidic environment, Yb^{3+}, Sm^{3+} and especially Eu^{3+} are reduced to a bivalent state with Eu^{2+} becoming a complete geochemical analogue of Sr^{2+} and being separated from the other rare-earth elements. This is a manifestation of a specific Eu geochemistry;

(5) differences in sorption capacity contribute to the separation of TR_{Ce} and TR_Y; sorption capacity decreases from La to Lu;

(6) differences in the ability to form organometallic compounds lead to the accumulation of Y and TR_Y in caustobioliths and black shales rich in organic matter.

Approximately 300 minerals containing the rare-earth elements are known but only 20 minerals are economically valuable. The most important of these are monazite (Ce, Th) $[PO_4]$ (54-70% TR_2O_3), xenotime Y$[PO_4]$ (51-60%), churchite (Ce, Y)$[PO_4]2H_2O$ (42-59%), bastnaesite (La, Ce)$[CO_3]F$ (65-75%), parisite $Ce_2Ca[CO_3]_2F_2$ (46-60%), yttrosynchysite (doverite) $YCa[CO_3]_2F$ (45%), loparite (Ce, Na)(Ti, Nb, Ta)O_3 (31-35%), and fergusonite Y$[NbO_4]$ (30-45%).

METALLOGENY

Deposits of the rare-earth elements are formed in relation to post-magmatic products of primarily alkali magmas of the late stage of a geosynclinal cycle, as well as to alkali magmatism and metasomatism during the reactivation stages of a platform cycle. Abundant abyssal granite pegmatites with monazite and orthite, metamorphosed placers with brannerite, crystalline schists, gneisses and conglomerates enriched in monazite, orthite and rare-earth-bearing sphene are widely distributed in the Archean and Lower Proterozoic. Starting from the Middle and Late Proterozoic and throughout the Phanerozoic alkali magmatism was developing in relation to deep-seated faults, with which most of the rare-earth deposits are associated. As a result, ultrabasic-alkaline complexes, carbonatites and feldspathic metasomatites were formed within the shields, ore productive gabbroid-alkaline rocks accompanied by shonkinite and monzonite – in rigid median massifs, and syenites, granosyenites and alkali granites – in areas of consolidated folding. The differences in the composition of parent intrusive rocks, in depth and in temperature of formation, and the variable composition of the wall rocks are responsible for a great variety of rare-earth deposits which may contain Nb, Zr, Mo, Th, U, F, and occasionally Sr and Ba as by-products. In other cases, rare earths are by-products in the mining of thorium-uranium, tantalum-niobium, iron, fluorite and phosphate deposits. Accumulations of phosphatized fish bones enriched in rare earths and sometimes in uranium are found in platform sedimentary strata of Carboniferous, Permian and Tertiary age. Monazite or monazite-zircon-ilmenite placers are widespread in sea-beach marine facies of Tertiary and Recent deposits.

TYPES OF COMMERCIAL DEPOSITS

Of a great variety of rare-earth deposits the most important ones are described below. These are: (1) magmatic; (2) feldspathic

metasomatites; (3) skarn; (4) carbonatites; (5) hydrothermal plutonogenic; (6) placers; and (7) sedimentary deposits.

MAGMATIC DEPOSITS

Primary deposits of this origin are represented by loparite-bearing stratified massifs of urtite-foyaite-lujavrite rocks (see "Niobium and Tantalum Deposits") in which loparite is the principal ore mineral. Another example is the apatite-nepheline rocks of the Khibiny pluton in the Kola Peninsula, USSR, where rare earths are recovered from apatite processed for phosphorous fertilizers. So, magmatic types of rare-earth-bearing deposits are associated with agpaitic nepheline syenites.

DEPOSITS OF FELDSPATHIC METASOMATITES

Rare earths may be extracted as a by-product from tantalum-niobium deposits represented by feldspathic metasomatites and similar to them albitized alkali granites (see "Niobium and Tantalum Deposits"). They are contained in tantalo-niobates – fergusonite, rare-earth-bearing pyrochlore – marignacite, fluorides (fluocerite, gagarinite, etc.), and less frequently in silicates (gadolinite and others).

Albitites associated with granosyenites, alkali granites, syenites, and alkali syenites represent a special formation of rare-earth deposits. The composition of the rare-earth element group in albitites depends on alkalinity and nature of parent rocks, as well as on the composition of metasedimentary country rocks. The TR_Y/TR_{Ce} ratio increases with the transition from the central parts of albitites to their apical parts and contact zones. The elements of the TR_{Ce} group are usually prevailing where metasomatism was developed in the more basic host rocks. In the case of more acidic aluminosilicate host rocks the TR_Y group predominates. In such deposits, the rare-earth-bearing minerals are fergusonite, priorite, TR-pyrochlore, monazite, xenotime, fluorides, and fluocarbonates, as well as britholite, orthite, chevkinite, gadolinite, thalenite, yttrialite, and TR-malacon. Along with the disseminated

mineralization, ore occurs in stringers and in extremely enriched veins frequently reaching 1 m and more in thickness consisting in some localities of TR-pyrochlore, and in the others of malacon, riebeckite and priorite, or pure britholite.

SKARN AND OTHER CONTACT-TYPE DEPOSITS

Deposits of this type occur where alkali granites or syenites are intruded in limestones. Rare-earth-bearing skarn deposits in Sweden (Vilgelm, Bastnäs, Ostanmossen) may serve as an example. They are represented by andradite and sphene-bearing magnetite, actinolite and tremolite-actinolite skarns developed after Archean marbles or dolomitized limestones surrounding the massifs of alkali granitoid rocks. Skarns may contain britholite, cerite, orthite, bastnaesite and lanthanite. Compositionally similar to skarns are contact-type metasomatites formed at the contacts of alkali granites and basic pegmatites. An example of these is the Scrub Oakes Mine (Morris County, New Jersey, USA) where magnetite-hematite ores contain fluocarbonates of the rare-earth elements (yttrosynchysite, bastnaesite), monazite, xenotime, and chevkinite. The $TR_2O_3 + Y_2O_3$ content in the ores varies from 0.2 to 5.5% averaging 1.5%. The rare-earth elements resources are estimated at a few million tons.

CARBONATITE DEPOSITS

Most of the deposits of this type are multi-phase ones with the early calcitic carbonatites enriched in apatite and pyrochlore (with 0.1-0.2% TR_2O_3 in calcite) being frequently replaced by the late ankeritic carbonatites with rare earths released from calcite to form their own minerals – bastnaesite, parisite, ancylite, and more rarely monazite containing no Th. These minerals are closely associated with fluorite and sometimes with strontianite, barite and sulfides. The TR_2O_3 content in carbonatites of this type amounts to 1-3% increasing greatly up to 8-10% and more in the products of their weathering. Such deposits are distinguished

by an exceptionally cerium-group assemblage of the rare-earth elements. In some rare cases ankerite bodies with the rare-earth elements extend beyond the massifs of ultrabasic-alkaline rocks, localizing along extensions of the massifs or in the adjacent fault zones.

HYDROTHERMAL PLUTONOGENIC DEPOSITS

Three ore formations can be distinguished in the deposits of this type: (1) carbonate-barite-bastnaesite, (2) fluorite-bastnaesite-iron ore, and (3) rare-earth-base metal ore.

Deposits of Carbonate-barite-bastnaesite Formation

MOUNTAIN PASS. The deposit is situated in the San Bernandino County in California, USA. This largest known rare-earth deposit is a typical example of the considered ore formation. Many investigators classify it as a carbonatite one. Unlike carbonatites which occur within platform regions, this deposit is localized in a median massif of Precambrian folded rocks. It is related to essentially potassic alkaline rocks probably of a gabbroid family—shonkinites grading to syenites and alkali granites 900-1 000 m.y. in age. Ore bodies are represented by an irregular accumulation 230 m by 800 m in size, veins exceeding 200 in number, and brecciated mineralized zones of fenitized gneisses (Fig. 108). Ore bodies consist of calcite, less commonly dolomite and siderite (averaging 60%), barite (20%), bastnaesite (5-15%, in some bodies up to 60%), celestite and silicates (crocidolite, orthite, thorite and others). Fluorite, apatite, galena and monazite are present. The deposit is intensely exploited accounting for approximately 66 per cent of the total world production of the rare-earth elements.

Deposits of Fluorite-bastnaesite-iron Ore Formation

BAYAN OBO. The deposit is situated in Inner Mongolia, China, in the junction of the Archean crystalline basement with the Hercynian geosyncline-fold area. It is localized in Upper Proterozoic dolomitized limestones (1 400 m.y.). Biotite-bearing gra-

nites, granosyenites and syenites, 350 m.y. in age, outcrop nearby. The ore bodies are lenticular, extending for distances of up to one kilometre and dipping at 50-80°. The deposits consist of banded, stringed, and more rarely disseminated and massive magnetite and magnetite-hematite ores grading to amphibole-phlogopite-magnetite and aegirine-magnetite ores. In the central part of the deposit the magnetite ore is abundant in stringers and bands of dark-violet fluorite and bastnaesite with monazite and barite, which give the ore a characteristic banded structure. Fluorite-bastnaesite-hematite ores enriched in rare earths occur in the footwall of the bodies. Aegirinization is widely developed along the outer contacts, and the rocks there are in some places transformed to aegirinites which have a variable mineral composition and may include tantalo-niobates (pyrochlore, aeschynite), barium-titanium minerals (bafertisite and others), and rare-earth silicates (britholite, orthite and others).

Geochemically, the deposit is distinguished by high concentrations of Fe, Ba, Sr, TR_{Ce}, Ti, Nb, P, and F. The bastnaesite content is 6-10% within the limits of commercial iron ore. Fluorite-phlogopite-britholite and magnetite-apatite-britholite metasomatic bodies occur in the contact zones of granosyenites.

The history of the deposit's formation consists of a premineralization period, including the stages during which magnesian skarns, limestone skarns and britholite metasomatites were formed, and a mineralization period including monazite-magnetite, fluorite-bastnaesite-hematite, aegirine and sulfide stages. No agreement has been reached so far regarding the genesis of the deposit; some investigators believe that it is of hydrothermal, and the others of hydrothermal-metamorphic origin. According to the latter viewpoint, iron ore was formed as a result of metamorphism of originally sedimentary rocks, and rare-earth-fluorite mineralization was introduced into it by hydrothermal solutions.

Deposits of Rare-earth-base Metal Ore Formation

A typical deposit of this formation occurs normally in highly metamorphosed ancient
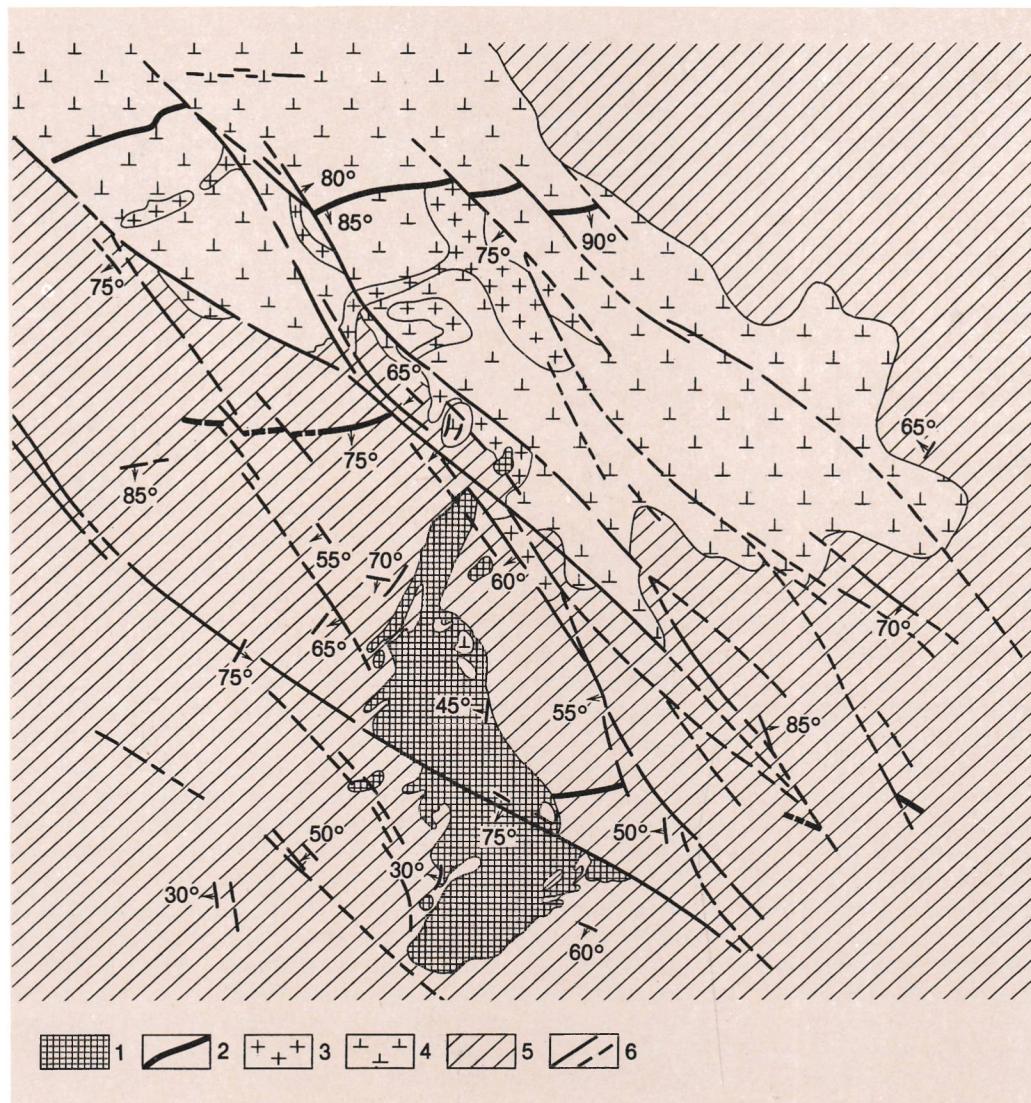
Fig. 108. Schematic geological map of a portion of the Mountain Pass deposit. (After J. Olson et al.):

1 – carbonate rocks of the Sulfide Queen ore body;
2 – shonkinite dikes;
3 – potassium granite;

4 – syenite-shonkinite;
5 – gneiss;
6 – fault (*a* – proved; *b* – inferred)

gneisses and epidote-actinolite schists. It is confined to a deep-seated fault accompanied by branching and intersecting faults. The areas where the faults join or intersect enclose vertical pipe-like granophyre bodies – satellites of a Late Hercynian fissure-type intrusion of subalkali granites. Grano-phyre pipes occupying a few hundred m^2 to 1 km^2 are surrounded by brecciated rocks whose fragments are often cemented with granophire, syenite-aplite and albitite. V. Nevskii regards them to be volcanic pipes.

Granophyres enclose very large cores of quartz pierced by granophyre veinlets. The cores are believed to be pre-granophyre formations – remnants of previously existing thick quartz veins. The rocks composing the
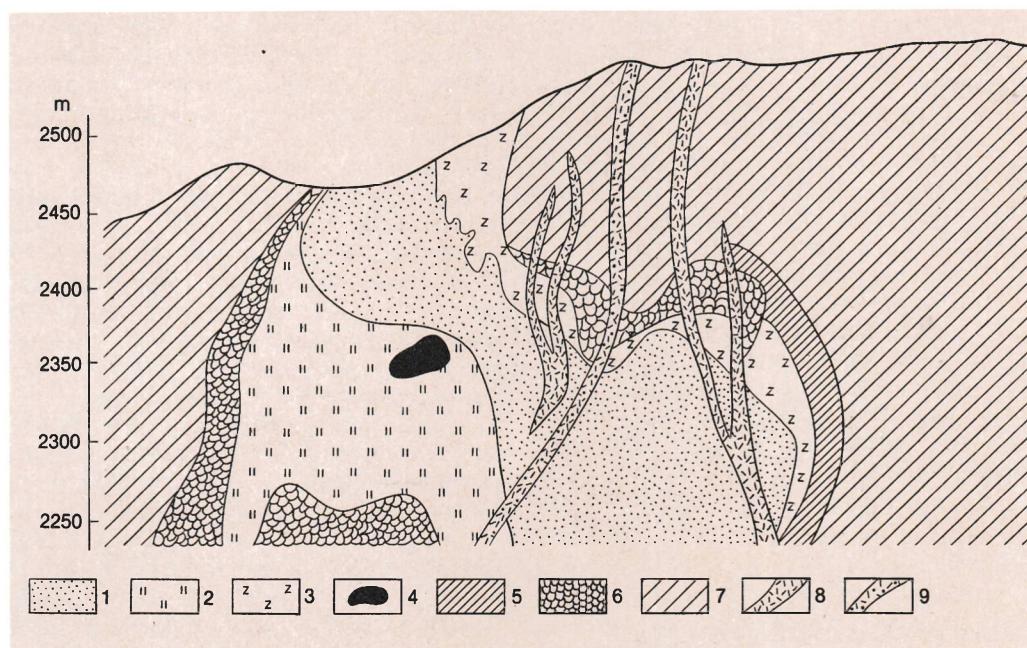
Fig. 109. Geological section across a granophyre pipe carrying rare-earth and base-metal mineralization:

1 – secondary quartzite after granophyre;
2 – quartz-chlorite rocks;
3 – biotite hornfels;
4 – monomineral quartz;
5 – hydrothermally altered green schists;

6 – brecciated schists;
7 – amphibole schists;
8 – diabase porphyry dikes;
9 – andesite porphyry dikes

pipes are strongly altered by hydrothermal processes; they are albitized, sericitized and silicified to secondary quartzites, and also biotitized and chloritized. The pipes have a zonal-concentric structure. The peripheral zone consists of fractured and brecciated schists which are succeeded inwards by biotite hornfels, quartz-chlorite-sericite rocks and secondary quartzites which include blocks of pre-granophyre quartz (Fig. 109).

Variations in the mineral composition of the zones is accounted for by the difference in the parent rocks after which hydrothermal processes acted – biotite hornfels developed after actinolite schists, and secondary quartzites after granophyres. All the rocks are pierced by quartz-carbonate-fluorite stringers. The ore minerals are yttrosynchysite, fluocerite, yttrofluorite, xenotime, monazite, malacon and thorite enriched in rare earths, galena, pyrite, and less frequently molybdenite. The minerals are arranged in successive vertical zones.

The content of base metals decreases, and that of rare earths increases with depth. Malacon becomes more abundant with depth; the assemblage of rare-earth minerals also changes notably – fluocarbonates of the rare-earth elements are replaced by fluorides which are succeeded by phosphates and farther downwards by silicates. The average ratio of $TR_Y : TR_{Ce}$ in the ores is equal 1.

PLACER DEPOSITS

One of the world's important sources of rare earths are placers of monazite, xenotime, to a lesser degree fergusonite, euxenite, chirchite, and very rare placers of bastnaesite. Monazite is the most common rare-earth mineral found in seabeach placers, e. g. in Korean People's Democratic Republic, Brazil, Indonesia and India. Rare-earth minerals other than monazite are found in alluvial-diluvial placers. Significant amounts of monazite are extracted as a by-product from zircon-ilmenite placers in Australia, India,

Thailand and the USA (see the chapters "Deposits of Thorium, Titanium and Zirconium").

SEDIMENTARY DEPOSITS

A peculiar source of rare earths are accumulations of phosphatized fish bones occurring in platform deposits – sediments of shelf zones of Late Carboniferous, Early Permian and Tertiary epicontinental seas. The deposits consist of flat-lying aleurolitic clays interbedded by marls and including intercalations of black clays abundant in bone detritus (30 and sometimes 80%) and pyrite-melnikovite. Fish remnants – fossilized fish bones, shark teeth, fins and scales – contain, apart from uranium, up to 5-12% P_2O_5 and 0.3-2% TR_2O_3 with the ratio TR_{Ce}/TR_Y close to 1 (see "Uranium Deposits").

24 SCANDIUM DEPOSITS

Scandium as a new element having the properties similar to boron was predicted and described as eka-boron by D. Mendeleyev in 1871. It was discovered by L. Nilson in 1879 who isolated its oxide from euxenite and gadolinite. It was only in 1937 that scandium was obtained as a metal. Until now it has only minor industrial applications, though some of its properties indicate that it may be of use in future. It is similar to aluminium in density but its melting point is 2.5 times as high, which allows it to be considered as a potential material for aircraft and rocket industry. The oxide is used in low-inductance ferrites used in computer memories. The radioactive isotope ^{46}Sc is used as a tracer of fluid flow.

Scandium is a commodity whose statistics of production is quoted in kilograms, and that of demand expected by the year of 2000 – in dozens of kilograms. The price of 1 kg of metal is 45000 US dollars. The crustal abundance of scandium is $6 \cdot 10^{-4}\%$. The concentration factor is ~150.

Scandium is a lithophile element similar in its geochemical behaviour to TR_Y^{3+}, less so to Zr^{4+}, and to Fe^{2+} and Mg^{2+} as rock-forming elements. Therefore scandium tends to be dispersed. In dark-coloured minerals (pyroxenes, amphiboles, biotites) it

substitutes Fe^{2+} and Mg^{2+} isomorphously, and where rare earths, especially TR_Y are present, it is captured by them. The highest scandium concentrations are related to high-temperature post-magmatic processes of granite magmas, especially where they develop in basic rocks. Scandium is easily transportable in the form of complex compounds whose migration capacity is even higher than that of the rare-earth elements. Under hypergenetic conditions scandium is released from most of the minerals and being a rather strong base – "hydrolyzate" – accumulates together with aluminium in bauxites (as a constituent of leptochlorites) and in various phosphate compounds together with the rare-earth elements.

Scandium forms two very rare minerals: thortveitite $Sc_2[Si_2O_7]$ (53% Sc_2O_3) and sterrettite $Sc[PO_4] \cdot 2H_2O$ (39%). Another scandium-bearing mineral, bazzite, which is an analogue of beryl is also known. Gadolinite, euxenite, khlopinite, orthite and davidite contain scandium in the amounts of 1-2%, and xenotime, wolframite, zircon, cassiterite, brannerite, beryl and ferrimuscovite in the amounts of less than 0.1%.

Scandium is extracted in small amounts from thortveitite which is very rarely found in rare-earth-bearing granite pegmatites occurring mainly in basic rocks (the Iveland deposit in Norway). Thortveitite is formed at the early stage of a pegmatite process. Its accompanying minerals (euxenite, samarskite, xenotime and biotite) are usually also enriched in scandium.

The world production of scandium is based on its extraction as a by-product from the processing of wolframite, cassiterite, rare-earth minerals (euxenite, xenotime, etc.) and partially uranium (davidite, brannerite) concentrates, and phosphatized bone remnants. The Sc_2O_3 content in phosphorites may be as high as 0.04%. Besides, scandium accumulates in coal ash. Should the need for scandium increase significantly, it could be produced as a by-product during processing of titanomagnetite and zircon concentrates, from the waste products of the aluminium industry and from coal ash. The production of scandium from the waste products of the processing of wolframite concentrates could

be profitable if they contain 0.04-0.05% Sc. The same applies to slags after processing of cassiterite concentrates if they contain 0.1% Sc, and the zirconium content is not higher than 0.3%.

25 GERMANIUM DEPOSITS

In 1871 D. Mendeleyev predicted a new element resembling silicon, which he described as eka-silicon. The element was discovered in 1886 by the German chemist C. Winkler in the mineral argyrodite. Being an excellent semiconductor, germanium is widely used in radioelectronics. It is also used to produce lenses in infrared optics and in the other fields of modern technology. The production of germanium in the capitalist countries in the seventies was 60 tons (exclusive of use of a secondary metal) with the potential demand by the year of 2000 of 100 tons. The price of 1 kg of refined germanium was 295 US dollars in 1976.

The production of germanium is based on specific germanium minerals like germanite ore, and on its extraction as a by-product from sulfide ores and coals. In future germanium might be recovered from certain types of iron ore. Large germanium-bearing deposits must have the reserves of more than 3-4 thousand tons, and ordinary ones – approximately 500 tons.

GEOCHEMISTRY AND MINERALOGY

Germanium has five stable isotopes ^{70}Ge (20.52%), ^{72}Ge (27.43%), ^{73}Ge (7.76%), ^{74}Ge (36.54%), and ^{76}Ge (7.76%). The crustal abundance of germanium is $1.4 \cdot 10^{-4}\%$, and the concentration factor is 150.

In the four-valence state germanium is a complete geochemical analogue of Si^{4+}. Therefore, in the presence of Si^{4+} it is always dispersed and is an isomorphous constituent of silicates. A small amount of germanium accumulates in post-magmatic products associated with granite magmas (pegmatites and greisens), especially where fluorine is abundant. Topaz, lithium-bearing micas, spodumene, tourmaline and other minerals contain high amounts of germanium (up to 0.01% Ge). It becomes bivalent

in a reducing environment exhibiting geochemical coherence with Fe^{2+} and Zn^{2+} and being dispersed either in iron-bearing minerals (pyrite, chalcopyrite, bornite, magnetite), or in sphalerite and wurtzite.

The most significant feature in the geochemistry of germanium is its triform nature. It is lithophile and is always dispersed in oxidizing environment, and siderophile and chalcophile in a reducing environment.

Germanium is able to concentrate only where its petrogenic analogue, silicon, is absent. This is why high concentrations of germanium are commonly found in endogenous deposits which do not contain silicates and are localized in carbonate rocks devoid of iron concentrations. Germanium-rich minerals occur in sulfide ores lying in limestones with Ge^{2+} being dispersed in sphalerite or chalcopyrite. Germanium substitutes Fe^{2+} in chalcopyrite to form germanite $Cu_2(Cu, Ge, Fe)_2S_4$ or renierite $(Cu, Fe)_2(Fe, Ge)_2S_4$ – the minerals containing 5-10% Ge. In a sulfide process Ge^{4+} is similar to As^{3+} and As^{5+} in its geochemical behaviour. This explains its presence in sulfosalts – enargite, luzonite and tennantite. Due to the existence at low pressure of the $[GeS_4]^{4-}$ and $[GeS_6]^{8-}$ complexes which are precipitated by arsenic, argyrodite and canfieldite – $Ag_8[GeS_6]$ – appear in near-surface deposits.

Under hypergene conditions, easily soluble alkali germanates are formed in the form of which germanium is depleted and, in rare cases, is deposited in the oxidized zone in the form of iron germanates (stottite) or complex germanates-sulphates (fleischerite, itoite).

Germanium has a strong sorption capacity and a tendency to form germanium-organic compounds – humates. It is taken up from solutions by organic substances, especially at a stage of peat formation, and accumulates later in coals.

METALLOGENY

The oldest germanium concentrations are associated with iron quartzites formed in Precambrian geosynclinal troughs with intense underwater volcanism. Germanium-rich copper-lead-zinc ores of Tsumeb (Na-

mibia) and Kipushi (Zaire) were formed in the carbonate rocks of the African shield in the Late Proterozoic (630 m. y.). Stratiform lead-zinc deposits, also enriched in germanium, were formed in thin-bedded dolomites and limestones in a platform sedimentary cover during the Phanerozoic time. Coal deposits are formed in the depressions developed within the platforms, and germanium accumulates in coals after it is released from bedrocks and ores and is transported along paleovalleys. The richest germanium deposits which were formed during the Kimmerian and Alpine epochs are confined to the Pacific Ore Belt (deposits of Bolivia, Japan, etc.) and to the East Alpine province of the Mediterranean Belt (Reible, Bleiberg, etc.). In the East Alpine province, the concentration of germanium in sphalerite amounts to 500 ppm. The youngest germanium deposits are lignites in Japan.

TYPES OF COMMERCIAL DEPOSITS

Economically recoverable germanium concentrations are found in two types of ores: hydrothermal and sedimentary.

HYDROTHERMAL DEPOSITS

The principal factors governing the distribution and concentration of germanium in hydrothermal sulfide deposits are: (1) apart from the specific germanium minerals, germanite, renierite, argyrodite, and canfieldite, the most important germanium concentrate is sphalerite. The average germanium abundance in sphalerite is 43 ppm, and the highest is 550 ppm as estimated by V. Ivanov; (2) germanium accumulates in late-stage and low-temperature sphalerite varieties, orange and reddish cleiophanes, and in colloform modifications; (3) sphalerites from deposits in carbonate rocks are commonly enriched in germanium; (4) germanium is relatively highly concentrated in the deposits of copper-arsenic mineral assemblage (enargite-tennantite); (5) gallium is commonly found to be concentrated in sphalerite together with Ge.

The most interesting groups of sulfide deposits are: plutonogenic hydrothermal (germanite-renierite ores of a galena-sphalerite-chalcopyrite formation, e.g. Tsumeb in Namibia and Kipushi in Zaire); volcanogenic hydrothermal (near surface deposits of a cassiterite-argentite formation in quartz-porphyry stocks, e.g. Potosí in Bolivia); stratiform (galena-sphalerite deposits in carbonate rocks, e.g. Missouri province); and massive sulfide (massive copper-zinc sulfide ores). Below follows the description of the specific germanium deposits.

TSUMEB. Tsumeb is the largest in Africa, unique copper-lead-zinc deposit rich in Ag, Cd, Ge, and Ga. It is situated in Namibia, 380 km north of Windhoek. The deposit has been mined since 1907. It lies in Precambrian platform-type strata of the Otavi series covering unconformably old granite-gneisses and crystalline schists which form an extensive brachysincline. The host rocks are thin-bedded dolomites of the upper Tsumeb substage.

The deposit is a steeply dipping pipe-like body (Fig. 110) cutting a dolomitic sequence in the brachysyncline limb and extending to a depth of more than 1 km. The central part of the body consists of the quartz core and feldspar replaced by sericite with sparse sulfide dissemination surrounded by a shell of massive sulfide ores – galena, enargite, sphalerite, grey copper ore, and hypogenic chalcocite, as well as germanite and renierite. The content of germanium minerals is 10-20% occasionally reaching 50-60%. Germanite includes small-size gallite aggregates. Germanite is intensely replaced by renierite.

The deposit was formed in four stages: pyrite, bornite, gallite, germanite and sphalerite appeared at the first stage; sericite, quartz, calcite, enargite, luzonite, and tennantite – at the second; galena – at the third; and renierite and chalcocite were deposited at the fourth stage. Zones of oxidation and secondary enrichment which are distinguished by an unusual diversity of extremely rare minerals extend to a depth of 300 m. Of particular interest is the discovery of secondary germanium minerals – stottite $Fe^{2+}[Ge(OH)_6]$, fleischerite $Pb_3Ge^{2+}[(SO_4)_2(OH)_4]\cdot4H_2O$, and

Fig. 110. Geological section of the Tsumeb deposit, Namibia. (After P. Söhnge):

1 – main ore body;
2 – quartz-feldspar aggregate replaced by sericite ("pseudoaplite");
3 – quartzites and arkoses of the Mulden series;
4-6 – upper Tsumeb substage:
4 – light coloured, thin-bedded dolomite with oölitic chert intercalations;
5 – dark, thin-bedded dolomite with limestone, shale and oölitic chert interbeddings;
6 – light coloured, thick-bedded dolomite with numerous chert interbeddings;
7 – fault
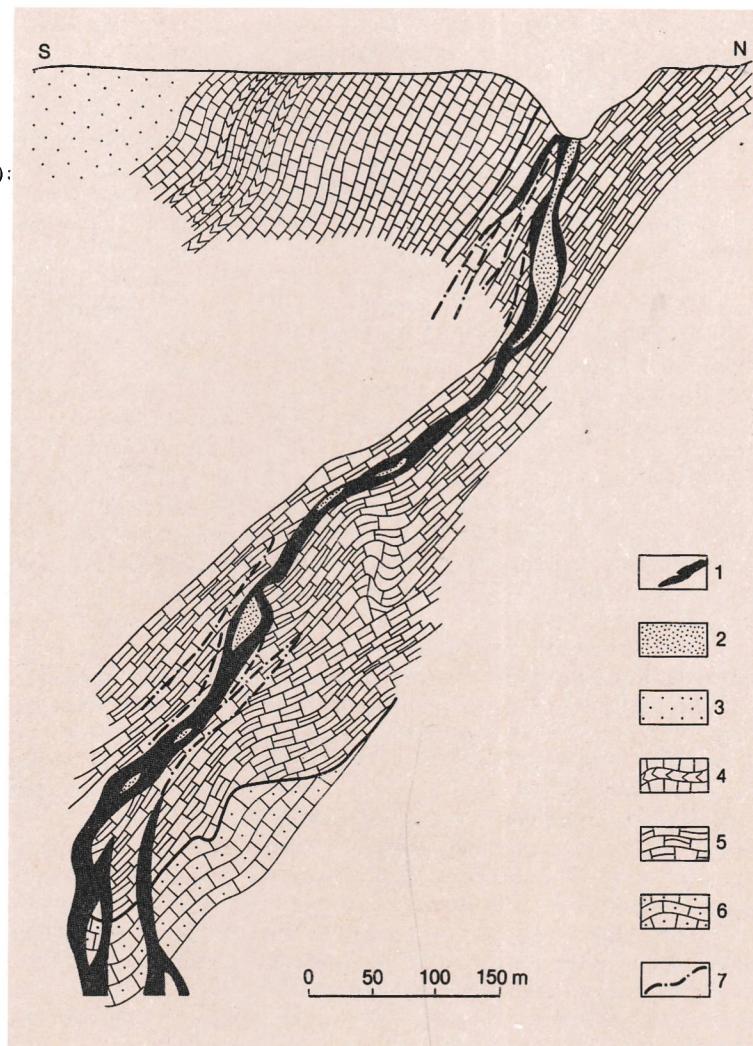
itoite $Pb_3[Ge(SO_4)_2(OH)_2O_2]$. Concentrates containing 0.5% Ge are recovered from the ores of the deposit.

SEDIMENTARY DEPOSITS

The sedimentary germanium-bearing deposits are represented by coal beds and iron ores.

DEPOSITS OF GERMANIUM-BEARING COAL BEDS. Germanium can be extracted as a by-product from coking coal in the coking process in which a part of germanium passes into supernatant water, and the other part becomes volatile and escapes. Besides, germanium is recovered from industrial coal ash. Brown coals containing more than 0.5 kg Ge per ton of ash are considered to be a high-grade commercially valuable material, and those containing about 50 g Ge per ton are qualified as low grade. Deposits containing up to 10 kg germanium per ton are considered as unique. The following main factors are governing the concentration and distribution of germanium in coal beds.

(1) Germanium concentration in coal beds is related with inflow of Ge to ancient peat bogs by water streams from areas containing the germanium-rich source material – volcanogenic-sedimentary rocks, iron

quartzites, and sulfide ores. Besides, some amount of germanium is concentrated during diagenesis.

(2) Coal beds formed under different geological conditions vary in the germanium content. The highest Ge concentrations are found in coal basins situated in intermontane basins of young mobile regions – East Transbaikal region, Sakhalin, Primorskii Krai (Pacific coast of the USSR), Central Asia, Japan.

(3) Coal beds of fluvial origin contain approximately ten times as much Ge as coal beds of lacustrine origin, and the highest concentrations are found in the deltas of rivers.

(4) Germanium is distributed unevenly within coal basins. The highest concentrations are observed in the peripheral portions located in the vicinity of the source area, and in paleovalleys along which germanium was transported by water.

(5) The germanium content of coal beds is highest in the uppermost or lowermost parts of individual coal seams as compared with the middle portions. This is why the highest Ge concentrations are found in thin coal seams in many basins.

(6) High germanium concentrations are usually observed in strongly gelified coals rich in virain and containing high percentages of humic acids and humates.

(7) The higher is the degree of coal metamorphism, the lower is the Ge content. This is explained by the action of aggressive, oxygen-rich underground water which oxidizes humates and removes the released germanium. In fact, pit waters in some coal basins are relatively high in Ge.

DEPOSITS OF GERMANIUM-BEARING IRON ORES. Germanium is relatively highly concentrated in volcanogenic-sedimentary deposits and in metamorphogenic iron quartzites which were produced by the metamorphism of volcanogenic-sedimentary formations. The former contain 30-60 ppm Ge, and the latter 5-15 ppm. In the process of iron ores smelting germanium passes into slags from which it can be extracted. The principal mechanisms of the distribution and concentration of germanium in iron ores are as follows (V. Grigoriev, 1971).

(1) Germanium-rich iron ores were formed during the epochs of most active volcanism (Early Proterozoic, Devonian-Carboniferous, Jurassic-Cretaceous) when underwater volcanoes erupted and supplied germanium compounds into sea water. These compounds were captured by coagulating suspensions of Fe and Mn carbonates and hydroxides. Some quantity of germanium might be supplied into sea basins with the ash material of surface volcanoes. And finally, Ge might be supplied by surface waters leaching it from various rocks, primarily from surface volcanics. Germanium concentrations are predominantly associated with acidic volcanism.

(2) The highest Ge concentrations are observed in iron ore deposits of the Atasuiskii type localized in red volcanogenic-sedimentary ferriferous-silicic-carbonate rocks in which magnetite-hematite ores are interstratified with jaspers. The highest Ge concentrations are confined to magnetite-siderite facies deposited in highly reducing environments. Germanium concentrates in Fe^{2+}-bearing minerals – siderite and iron chlorites. The Ge content increases when subject to metamorphism siderite is transformed to magnetite.

(3) Magnetite is the principal germanium carrier (50-60 ppm). Where it has been subject to martitization magnetite contains much less germanium (20 ppm). The iron-bearing minerals other than magnetite (chlorites, amphiboles, hematite) contain lesser quantities of germanium. Any oxidation processes promote germanium removal.

(4) The accumulation of germanium in iron formations was favoured by the reducing environment which existed in the Early Proterozoic. The highest Ge concentrations are observed in the vicinity of the manifestations of underwater volcanism. The development of the subsequent processes of alkali metasomatism lead to the redistribution of germanium – its removal from magnetite and accumulation in alkali amphiboles and pyroxenes. In the process of ancient weathering and oxidation of magnetite-bearing quartzites germanium was released from magnetite, and part of it accumulated in oxidized ores.

26 RHENIUM DEPOSITS

Rhenium, atomic number 75, was predicted by D. Mendeleyev in 1869, and was discovered in 1925 by the German geochemists Ida and Walter Noddack in columbite and gadolinite. In 1926 they isolated it in a free state, and in 1928 they established that rhenium is most concentrated in molybdenite, and that it is a geochemical analogue of molybdenum.

Rhenium has a high melting point, high resistivity and hardness, and high module of elasticity; it is easily alloyed with Mo, Pt, Os, Co, V, W, Ta, and Nb, and is similar to platinum in many respects. It is used as an alloying element in superheat-resistant metals, and has a unique application as a catalyst in the petroleum-refining industry.

Rhenium production in the capitalist countries reached six tons by 1975. The price of rhenium is 1 200 to 2 000 US dollars per kilogram.

Rhenium is produced from the tailings resulting from the processing of molybdenite, copper-molybdenite, and copper concentrates. In the process of roasting the concentrates rhenium oxidizes to Re_2O_7 and escapes with flue dusts which are collected in the filters of roasting furnaces. The dusts contain 0.01-0.2% Re with its initial content in the concentrate being 0.005-0.05%. Normally, large deposits contain more than 30-40 tons of rhenium reserves, and small ones 3-5 tons.

In nature, rhenium is known to have two stable isotopes ^{185}Re (37.1%) and ^{187}Re (62.9%). Isotope ^{187}Re is radioactive (half-life $5 \cdot 10^{10}$-10^{11} years) and passes into ^{187}Os. The crustal abundance of rhenium is $7 \cdot 10^{-8}$%, and the concentration factor is within 1 000-10 000.

Rhenium is a chalcophile element intimately associated with molybdenum. It cannot form independent minerals in the presence of molybdenum being dispersed in molybdenite and relatively concentrated in late-stage low-temperature ores and in their latest generations. This explains why molybdenite from quartz-wolframite and quartz-molybdenite deposits contains 0.001-0.003% Re, while its content in the molybdenite of lower-temperature deposits

is an order higher. The average ratio Mo/Re = 5 000.

Rhenium has a marked geochemical affinity for copper; its highest concentrations are found in copper-molybdenum deposits. Where the molybdenum content is insignificant, rhenium accumulates to form its only specific mineral – dzhezkazganite $CuReS_4$ – containing approximately 55% Re.

Apart from molybdenite in which the average abundance of rhenium is 114 ppm, it is contained in chalcopyrite (0.6 ppm) and in pyrite (0.3 ppm). In pentlandite-chalcopyrite-pyrrhotite ores rhenium has some affinity for the platinum group elements and concentrates in pyrrhotite together with osmium and iridium.

In massive copper sulfide deposits rhenium concentrates in chalcopyrite and pyrite, and though its content is low the tonnages may be significant. Where massive sulfide ores were subject to metamorphism, rhenium is removed. High rhenium concentrations are found in copper-molybdenite deposits (400-900 ppm in molybdenite). Its highest concentrations (18 800 ppm) are confined to a rhombohedral beta-modification of molybdenite. In the deposits of this type, a direct correlation is observed between the rhenium and selenium contents in molybdenite.

Rhenium has a high migration capacity and is easily depleted in an oxidizing environment. It is most abundant in young Phanerozoic deposits. It concentrates in sedimentary deposits, e. g. in copper-bearing shales (Mansfeld, German Democratic Republic) and in cupriferous sandstones (Dzhezkazgan, Kazakhstan, USSR); rhenium-bearing ores are usually localized at the margins of depressions. Rhenium migrates in the form of anion $[ReO_4]^-$ and precipitates in a reducing environment together with Cu, Pb, and Zn under the action of H_2S. The distribution of rhenium in various minerals is dependent on the oxidation-reduction state and pH of the environment; chalcopyrite ores are low, and bornite ores are enriched in rhenium. It precipitates from acidic mineralizing solutions and easily migrates in alkaline environments. In the Dzhezkazgan deposit, rhenium is concentrated in bornite, bornite-chalcocite

and galena ores. Dzhezkazganite occurs in characteristic spotted ores localized at the contact of bornite-chalcopyrite and galena ores; apart from rhenium it is enriched in Ti, As, Co, Ni, V, and Mo.

Where sulfides were recrystallized and redeposited during epigenetic processes, rhenium is partially redistributed and removed. Rhenium is likely to accumulate biogenically under exogenic conditions. It is relatively concentrated in black bituminous shales and brown coals, especially where they were formed in areas of intense volcanic activity. Rhenium occurs in coals in the form of metallo-organic compounds. Some rhenium concentrations are found in uranium-molybdenum deposits of the Colorado type.

Thus, rhenium is a typical dispersed element concentrating in plutonogenic hydrothermal copper-molybdenum deposits and in sedimentary cupriferous sandstones and copper-bearing shales, from which it is extracted as a by-product in the complex processing of ores.

27 THALLIUM DEPOSITS

Thallium was discovered by means of the spectroscope in 1861 by the British scientist W. Crookes. It is similar to lead in physical properties. It is used in semiconductor devices, photosensitive cells, in exposure meters to detect infrared radiation, in fluorescence lamps, as activator in scintillation crystals, in alloys for abrasion-resistant bearings, in the preparation of heavy and immersion liquids, etc.

Despite a great variety of applications, the demand for thallium is relatively low chiefly because of the highly toxic nature of the metal and its compounds. The annual production of thallium in the capitalist countries is approximately 20 tons. The price of one kilogram of the thallium metal is 20 US dollars. The world production of thallium is based on the processing of sulfide ores of hydrothermal and massive sulfide deposits; thallium is extracted as a by-product from flue dusts of agglomeration and roasting, filter cakes, residue of sulphuric acid production, etc. Thallium can be extracted in small amounts from specific

minerals where its content in the ore is not less than 0.1%.

There are two naturally occurring stable isotopes of thallium, ^{203}Tl (29.50%) and ^{205}Tl (70.50%). The crustal abundance of thallium is $1 \cdot 10^{-4}\%$, and the concentration factor is $\sim 1\,000$.

The principal feature of thallium geochemical behaviour is that under natural processes it acts as a monovalent element whose ionic radius is similar to those of Rb^+ and K^+ and also of Pb^{2+}. As a consequence thallium is widely dispersed in minerals. Under some conditions it displays lithophile properties and under the others behaves as a chalcophile element. Resembling Rb^+ it concentrates together with it at the late stage of the pegmatite-forming process and in greisens entering the composition of lepidolite (up to 100-500 ppm), rubidium-bearing muscovite and pollucite, from which it can be extracted as a by-product of rubidium and cesium. Under hydrothermal sulfide process it is distributed between silicates (sericite, chlorite) and sulfides – galena, sphalerite, pyrite, marcasite and, to a lesser extent, chalcopyrite. Thus, the average Tl content in the ores cannot be used as the criteria of their evaluation for thallium; silicates in sulfide deposits are often more rich in thallium than sulfides. The highest Tl contents in sulfide ores are usually found in the deposits devoid of sericite and, in particular, in those localized in carbonate rocks.

Thallium has a certain geochemical affinity for arsenic and, to a lesser degree, for antimony. This affinity is manifested in its accumulation in the deposits enriched in these elements – in base-metal ores rich in Pb sulphosalts (meneghinite, geocronite, boulangerite, and others), in low-temperature Sb- and As-bearing mineral associations, and in combined occurrence of the three elements in pyrite and marcasite. Seven specific minerals of thallium originate in near-surface conditions under low H_2S partial pressure and high As and Sb potential. The most common of these are found in realgar deposits – lorandite $TlAsS_2$ (59%), vrbaite $TlAs_2SbS_5$ (29-32%), and hutchinsonite $PbTlAs_5S_9$ (18-25%). The deposits containing thallium minerals are

usually small in size and have low economic value.

Practically all of the thallium produced in the world is recovered from the complex processing of ores mined in hydrothermal, stratiform and massive sulfide deposits. The concentration of thallium in these deposits is a function of its specific properties – its variable (lithophile and chalcophile) nature, its ionic radius which is the largest known in chalcophile elements, and its affinity for arsenic and antimony. As a consequence thallium concentrates in most low-temperature base metal deposits enriched in sulphosalts, accumulates in the late generations of its concentrator minerals, and, having a high sorption capacity, is adsorbed by metacolloidal colloform ores (sphalerites and pyrites), e. g. Daraiso, Upper Kwaisa, Jijikrut in the USSR, and Olkusz in Poland. In the recrystallization of these ores thallium is removed and may precipitate in the form of independent minerals (e. g. in Jijikrut). Most enriched in thallium are the young deposits of the Mediterranean Belt (Balkan Mts., Carpathians, Caucasus, Central Asia, and East Transbaikal region).

Under hypergene processes, owing to the high solubility of its sulphates, thallium is removed from ores and may be adsorbed by limonites and manganese oxides or captured by jarosite; as a result of these processes bright-colour "thallium ochres" are produced in the host rocks. In sedimentary deposits thallium may concentrate in small amounts in manganese ores.

28 GALLIUM DEPOSITS

Gallium – an analogue of aluminium – was predicted in 1871 by D. Mendeleyev as eka-aluminium. It was discovered spectroscopically in sphalerite by P. Lecoq de Boisbaudran in 1875. Until recently its application was limited. It was used in low-melting alloys, heat-limiting devices, vacuum tubes (alloyed with Cd), and in special mirrors of high reflecting power. In the early seventies a great interest was attracted to gallium in connection with the use of its arsenides and phosphides as new semiconductors in computer ter-

minals – displays, in telemetry, and in laser technology. The production of gallium was estimated at 15 tons in 1975. The price of 1 kg Ga in 1975 was 210-220 US dollars. 90% of gallium produced in the world is recovered as a by-product from the processing of bauxite for aluminium, and 10% – from the residue of zinc production.

Gallium has two stable isotopes ^{69}Ga (60.4%) and ^{71}Ga (39.6%). The crustal abundance of gallium is $1.9 \cdot 10^{-3}\%$, and the concentration factor is 5-10.

The petrogenic analogue of gallium is aluminium, and where aluminium is present gallium is always dispersed being somewhat concentrated in the final, residual products of acidic and especially alkaline magmas – pegmatites. The highest concentrations were recorded in pegmatites of agpaitic nepheline syenites – in natrolite (up to 1 000 ppm), hackmanite (300 ppm), sodalite, and in nepheline (on average 57 ppm). Gallium is relatively concentrated in the minerals of rare-metal granite pegmatites – spodumene (10-700 ppm), lepidolite (10-300 ppm) and beryl.

Apart from being a lithophile element, gallium acts as a chalcophile element in sulfide hydrothermal environment. It enters the composition of alumosilicates (sericite, chlorite, tourmaline), and sphalerite (41 ppm), wurtzite (112 ppm) and chalcopyrite (5 ppm). It accumulates in low-temperature lead-zinc deposits. The full similarity in behaviour of gallium in respect to germanium is observed under such conditions. The highest gallium concentrations are found in specific gallium deposits containing germanium ores. The Ga concentration in such deposits is sufficient to form the only known specific mineral of gallium – gallite $CuGaS_2$ (29-36%) (Tsumeb, Namibia; Kipushi, Zaire). Gallium can be relatively highly concentrated in sphalerites where its dispersion in alumosilicates is excluded, i. e. where the sulfide-forming process develops in carbonate rocks. Some quantity of gallium is present in spalerites of massive sulfide lead-zinc deposits, and tin deposits of a cassiterite-sulfide formation, in which gallium is concentrated in cassiterite.

In exogenous conditions gallium is a complete analogue and an associate of

aluminium. It enters the composition of bauxite jointly with aluminium, showing virtually invariable contents (20-90 ppm) irrespective of the age and origin of bauxite.

29 CADMIUM DEPOSITS

Cadmium was discovered by the German professor F. Stromeyer in 1817 in zinc ore. Because cadmium is not oxidized in the air its major use is in the electroplating of metal products to obtain superior corrosion resistance. Alloys of Cd and Cu are used to manufacture traction power-supply systems, various types of bearings, and structural elements of automobiles, airplanes and radio devices. It is used in nickel-cadmium and silver-cadmium batteries. Because of the high thermal neutron cross-section absorption of cadmium it is used to manufacture control rods for nuclear reactors. The cadmium production in the capitalist countries was 13.5 thousand tons in 1975. The probable demand by the year of 2000 is estimated at 25-45 thousand tons. In 1976 the price of cadmium was six US dollars per kilogram.

All commercial cadmium is recovered as a by-product from the tailings obtained in the refining of zinc, lead, and some copper sulfide ores.

Cadmium has eight stable isotopes: ^{106}Cd (1.22%), ^{108}Cd (0.87%), ^{110}Cd (12.39%), ^{111}Cd (12.75%), ^{112}Cd (24.07%), ^{113}Cd (12.26%), ^{114}Cd (28.86%), and ^{116}Cd (7.58%). The crustal abundance is $1 \cdot 10^{-10}\%$.

Cadmium is a typical dispersed chalcophile element, a geochemical analogue of zinc. In endogenous conditions it is always associated with zinc and concentrates in sphalerite which is the most important endogenous ore mineral of cadmium. The cadmium content of sphalerite is highly variable ranging from 0.01 to 2.4%. A Cd-rich sphalerite variety is known as přžibramite. The average abundance of cadmium in sphalerite is 0.286% from the data of V. Ivanov. It has been proven experimentally that the mixability of sphalerite and greenockite (CdS) is limited, and that of hexagonal ZnS modification, wurtzite and greenockite, is unlimited. The

cadmium content of wurtzite is 1-3.5% occasionally reaching 30% (Berenguela in Bolivia, Tsumeb in Namibia). Apart from sphalerite, cadmium is contained in chalcopyrite, stannite, galena, chalcocite, and bornite. The cadmium concentration varies with the type of mineralization (ore formation), metallogenic features of the provinces, and physico-chemical conditions of mineral deposits. The principal regularities of cadmium concentration are as follows (V. Ivanov, 1964).

(1) The average Cd percentages in sphalerite from different ore formations (in %) are: copper-molybdenum – 0.24, cassiterite-silicate-sulfide – 0.34, stratiform lead-zinc – 0.33, lead-zinc in skarn carbonate rocks – 0.5, lead-zinc in silicate rocks – 0.29, massive sulfide-base metal – 0.25, and silver and gold-silver – 0.7. The moderate-temperature deposits occurring in carbonate rocks are more abundant in cadmium than those in silicate rocks, which is accounted for by a more alkaline environment of mineralization favouring the concentration of cadmium in sphalerite.

(2) Cadmium is highly concentrated in near-surface volcanogenic hydrothermal deposits occurring in areas of intense volcanic activity and enriched in sulphosalts, silver, and occasionally in gold. In the Berenguela deposit (Bolivia), the cadmium content in conchoidal ores formed after wurtzite reaches 3-5% and is as high as 30% in the mineral itself. The relatively high Cd concentrations (1-2%) are found in Ag- and Au-bearing ores in the Balkan Mountains (Baia Sprie and Baia de Aries in Romania)

(3) Most abundant in cadmium are Phanerozoic deposits, especially those in areas of young volcanic activity. Examples are the deposits in Central Asia (Altyn-Topkan, Kurusai, Kansai), North Balkhash area, East Baikal region, Nogolnyi Range, Transcarpathia, and other areas in the USSR. The cadium-bearing provinces known in the world are the Erzgebirge (Freiberg, Přžibram, Clausthal), Upper Silesia, Great Britain (Flintshire, Derbyshire, etc.), Mexico (Santa Barbara, etc.).

(4) The concentration of cadmium is disturbed by the activity of Cl ions in mineralizing solutions because cadmium and

chlorine form stable soluble complexes preventing cadmium to enter the composition of sphalerite.

(5) In the hypergene zone, the routes of Zn and Cd migration separate rapidly; Zn forms easily soluble sulphates and is removed from the oxidized zone, and Cd forms six specific cadmium minerals. The major minerals are greenockite CdS (77.8%), otavite $CdCO_3$ (65.8%), and cadmoselite CdSe (47%). The minerals are of no economic value.

30 INDIUM DEPOSITS

Indium was discovered in 1863 by the German chemists F. Reich and T. Richter. Indium began to be used by the industry in 1930-1935 to obtain special bearing-metal alloys (with Ag, Pb, Cu, Cd, and Sn) and low-melting alloys (with Ga). In the last years it has been widely used in the electronic industry as a semiconductor metal. The In compounds with Sb are used as semiconductor materials which are capable to act as photoconductors in the infra-red region of the spectrum, and its compounds with As and P are used as thermoelements.

Indium is recovered as a by-product from the processing of lead-zinc, copper-lead-zinc and tin-lead-zinc ores.

The indium production in the capitalist and developing countries was 35-40 tons in 1978 with the potential demand estimated for the year of 2000 to be 75-130 tons. The price of 1 kg of indium (99.97% In) was 256 US dollars in 1976.

Indium has two stable isotopes [115]In (95.72%) and [113]In (4.28%). The crustal abundance of indium is $1.4 \cdot 10^{-5}$%, and the concentration factor is 1000-3000.

Like cadmium, indium is a typical dispersed chalcophile element. Geochemically, it is most closely associated with zinc but, unlike cadium, it displays some siderophile properties and has a clear geochemical coherence with tin.

The principal host minerals of indium are sphalerite, minerals of a sphalerite structure (chalcopyrite, stannite), and cassiterite. The

In abundances of these minerals as reported by V. Ivanov et al. (1966) are (in ppm): sphalerite – 40, cassiterite – 20, and chalcopyrite – 14.

The content of indium in sphalerite is related to the presence of iron in it. The most abundant in indium are iron-bearing sphalerites of moderate-temperature minerals, all other things being equal. The indium content in them decreases with the decreasing temperature of deposition and with lower iron content. The deposits localized in silicate rocks (more ferriferous) are usually more abundant in indium than those occurring in limestones.

The indium content is directly related to the tin content of sulfide deposits. Most abundant in indium are the deposits of a cassiterite-sulfide and cassiterite-silicate-sulfide formation. The indium content is highest in the near-surface wood tin deposits in acidic volcanic rocks (Jalinda, USSR). Colloform cassiterite in such deposits contains up to 1.35% In because of the presence of fine aggregates of some specific indium minerals recognized in the recent years.

These minerals are native indium, indite $FeIn_2S_4$ (59.3%), roquesite $CuInS_2$ (47.4%), and jalindite $In(OH)_3$ – an alteration product of indite.

The association of indium with tin is responsible for the metallogenic distribution of indium deposits. They are primarily found within the Pacific Ore Belt, and are of young, Kimmerian or Alpine age. Examples are indium-bearing provinces of the USSR Pacific coast (Lifudzin, Jalinda, Khingan and others), Northeastern territories (Valkumei, Omsukchan, etc.), Yakutia, East Baikal (Smirnovskii). They are also known in Bolivia (Santa Cruz, Poopo, Porco, etc.) and in Peru. Lesser indium concentrations are found in Hercynian provinces of tin-bearing sulfide ores.

Approximately 75% of the indium resources are found in lead-and-zinc deposits localized in silicate rocks, and 20% – in cassiterite-silicate-sulfide and cassiterite-sulfide-deposits, though the latter are more abundant in indium.

31 SELENIUM AND TELLURIUM DEPOSITS

Selenium and tellurium are geochemically similar elements. Tellurium was discovered in 1782 by the Austrian inspector of mines F. Müller von Reichenstein who examined the auriferous ores of Transylvania and was the first to assume the presence of a new element in them. His discovery was proved by M. Klaproth in 1789 who named the new element tellurium. Selenium was discovered 19 years later by J. Berzelius.

Until 1940 the use of both elements was limited. They were primarily used in the rubber, glass and chemical industries. Since the post-war time selenium has been widely used in semiconductor industry (for dc rectifiers), in photoelectric cells, meter instruments, television, and in indication systems. Tellurium is used in radio engineering (detectors), in thermocouples, semiconductor coolers and thermoelements. Both selenium and tellurium are also used in metallurgy as alloying additives in various steels and base-metal alloys. The selenium production in the capitalist countries reached 1 300 tons by 1977, and the production of tellurium has been kept at a level of 160-180 tons.

Selenium has six stable isotopes of mass numbers 74, 76, 77, 78, 80, and 82, and tellurium – eight isotopes of mass numbers 120, 122, 123, 124, 125, 126, 128, and 130. The crustal abundance (in $1 \cdot 10^{-4}\%$) is 0.05 for selenium and 0.001 for tellurium.

Selenium and tellurium are chalcophile elements; their widespread geochemical analogue is S^{2-}. Since the ratio S^{2-}/Se^{2-} in sulfides varies within 20 000 : 1 to 2 000 : 1, Se^{2-} is always dispersed in sulfides, and the formation of independent selenium minerals is possible in the environment of low sulphur potential. This is realized in arsenide and gold deposits, and in siderite-hematite veins. Being an isomorphous substitute for sulphur Se^{2-} concentrates in the latest sulfide generations. Various selenides may be produced by the disintegration of isomorphous S-Se series. Tellurium having larger ionic radius than selenium practically does not substitute for it and occurs in sulfide minerals in form of fine telluride inclusions.

Selenium is geochemically associated with Cu and to a lesser extent with Ag, Pb, Hg, Bi, Co, and Ni; tellurium is associated with Au and Bi. These associations are responsible for a great number of Cu, Ag, Pb, Bi, Co, and Ni selenides and Au, Ag, Bi and Pb tellurides. This also explains the concentration of selenium primarily in copper-nickel, copper-pyrite and cobalt-nickel deposits, and that of tellurium in low-temperature gold deposits.

Selenium is sufficiently volatile to accompany sulphur in volcanic gases. This explains why volcanic sulphur is always enriched in selenium.

The routes of S, Se and Te migration separate in the hypergene zone. Sulphur oxidized to a sulphate-ion migrates easily; Se^{2-} is oxidized to a selenite-ion at a higher oxygen potential and migrates in the alkaline environment. Where the mineralizing solutions become acidified, native selenium precipitates or is captured by iron hydroxides. A geochemical association of selenium with U, V, Mo and Cu is typical for the sedimentary process.

Selenium mineralization is developed at the margins of many deposits of uranium-bearing sandstones (e. g. the Colorado Plateau, USA). Selenium is also concentrated in black bituminous shales and in coal beds. Under these conditions tellurium is separated from sulphur and selenium. During the oxidation of sulfide deposits tellurium is adsorbed by iron hydroxides, and in gold-tellurium deposits passes into placers together with gold.

More than 40 minerals of selenium and the same number of tellurium minerals are known. In some cases the most significant of them which may be of practical value are: ferroselite $FeSe_2$ (68-72%), clausthalite $PbSe$ (27-28%), blockite $NiSe$ (68%), naumannite Ag_2Se (23-29%), tetradymite Bi_2Te_2S (36% Te), calaverite $AuTe_2$ (57%), altaite $PbTe$ (38%), and hessite Ag_2Te (62%).

The selenium and tellurium concentrations are associated with different metallogenic epochs; the older epochs are characterized by the dispersed form of both elements, and the younger epochs (Kimmerian and Alpine) by the occurrence of their own minerals. The latter are

commonly found in near-surface deposits formed in areas of young volcanic activity.

The most significant selenium and tellurium resources are confined to magmatic copper-nickel, hydrothermal copper-molybdenum, massive copper-sulfide, and infiltration selenium-uranium-vanadium deposits, from which almost all the selenium and tellurium produced in the world are recovered with their contents in the ores ranging within 0.04 to 0.004%. High-grade deposits consist of cobalt-selenium-tellurium ores (Akjilga, Kirghiz SSR and Verkhnii Seimchan, North-eastern territories, USSR), selenide ores (Pacajake, Bolivia; Sankt-Andreasberg, Federal Republic of Germany; Sierra de Umango, Argentina), uranium-

selenium ores (Shinkolobwe, Zaire; Lake Athabaska, Canada), and gold-telluride ores (Săcărimb, Fatza Baia, Romania). Below follows a brief description of the Pacajake deposit, an example of primary selenide ores; most of the other deposits are dealt with in the other chapters.

PACAJAKE. The deposit is localized in Devonian sandy shales being represented by a vein which extends for a few hundred metres. The vein consists of carbonates (siderite, calcite), barite and hematite. The essential ore mineral is blockite associated with clausthalite and naumannite. Pyrite is present as the product of the later-stage mineralization. The deposit was sporadically mined for silver.

REFERENCES TO "RARE ELEMENTS" SECTION

Albitized and Greisenized Granites (Apogranites). By A. A. Beus, E. A. Severov, A. A. Sitnin, and K. D. Subbotin. Moscow, USSR Academy of Sciences, 1962.

Atlas of Minerals and Ores of Rare Elements, Ed. A. I. Ginzburg. Moscow, Nedra, 1977.

Balashov, Yu. A. Geochemistry of Rare-earth Elements. Moscow, Nedra, 1977.

Beus, A. A., Dikov, Yu. P. Geochemistry of Beryllium in Endogenous Processes of Mineralization. Moscow, Nedra, 1967.

Borisenko, L. F. Scandium. Geochemistry, Mineralogy, and Genetic Types of Deposits. Moscow, USSR Academy of Sciences, 1961

Egel, L. E. Exogenous Deposits of Selenium. *Geology of Rare-element Deposits,* iss. 2, Moscow, Gosgeoltekhizdat, 1962.

Egel, L. E. Rare-earth Elements. *Evaluation of Mineral Deposits in Prospecting and Exploration,* iss. 21, Moscow, Gosgeoltekhizdat, 1963.

Frolov, A. A. The Structure and Mineralization of Carbonatite Massifs. Moscow, Nedra, 1975.

Gallium. By O. V. Vershkovskaya, V. S. Krasnova, V. S. Saltykova, A. E. Pervukhina. Moscow, USSR Academy of Sciences, 1960.

Genetic Types of Hydrothermal Beryllium Deposits. Ed. A. I. Ginzburg. Moscow, Nedra, 1975.

Genetic Types of Rare-element Deposits. Ed. A. I. Ginzburg. Ser. "Geology of Rare-element Deposits". Moscow, Gosgeoltekhizdat, 1961.

Geochemistry, Mineralogy and Genetic Types of Rare-element Deposits. Ed. K. A. Vlasov. V. 1, 1964; V. 2, 1964; V. 3, 1966. Moscow, Nedra.

Geology of Post-magmatic Thorium- and Rare-metal-bearing Deposits. Ed. V. A. Nevskii. Moscow, Atomizdat, 1972.

Ginzburg, A. I. Vertical Zoning of Rare-metal Deposits Associated with Granitoids. In: *Prognozirovanie skrytogo Orudeneniya* (Prognostication of Concealed Mineralization). Moscow, Nedra, 1976.

Ginzburg, A. I., Stavrov, O. D. Geochemistry of Cesium.–*Geokhimia,* No. 4, 1969.

Ginzburg, A. I., Ovchinnikov, L. N., Solodov, N. A. Genetic Types of Tantallum Deposits and Their Commercial Value.–*Geologia Rudnykh Mestorozhdenii,* No. 4, 1970.

Grigoriev, V. M. Mechanism of Germanium Distribution in Iron Ore Deposits. Moscow, Nedra, 1971.

Gurvich, S. I. Mechanism of Distribution of Rare-metal and Tin-bearing Placers. Moscow, Nedra, 1978.

Ivanov, V. V. Geochemistry of Dispersed Elements in Hydrothermal Deposits. Moscow, Nedra, 1966.

Ivanov, V. V., Poplavko, E. M., Gorokhova, V. N. Geochemistry of Rhenium. Moscow, Nauka, 1969.

Kaganovich, C. Ya. Zirconium and Hafnium. Moscow, USSR Academy of Sciences, 1962.

Kogan, B. I. Rare Metals. Moscow, Nauka, 1978.

Kogan, B. I., Nazvanova, V. A. Scandium. Moscow, USSR Academy of Sciences, 1963.

Kogan, B. I., Nazvanova, V. A., Solodov, N. A. Rubidium and Cesium. Moscow, USSR Academy of Sciences, 1971.

Kuzmenko, M. V., Eskova, E. M. Tantallum and Niobium. Moscow, Nauka, 1968.

Mechanisms of Formation of Hydrothermal Beryllium Deposits. Ed. A. I. Ginzburg. Moscow, Nedra, 1977.

Mineral Deposits of the USSR, V. 3. 2nd edition, revised and enlarged. Ed. Academician V. I. Smirnov. Moscow, Nedra, 1978.

Mineev, D. A. Lanthanides in Ores. Moscow, Nauka, 1974.

Minerals of Germanium and Their Deposits. Ed. A. I. Ginzburg. *Geology of Rare-element Deposits,* iss. 5. Moscow, Gosgeoltekhizdat, 1959.

Rare-earth Elements and Their Deposits. By A. I. Ginzburg, L. N. Zhuravleva, I. B. Ivanov, V. V. Shcherbina. *Geology of Rare-element Deposits*, iss. 3. Moscow, Gosgeoltekhizdat, 1959.

Rare-metal-bearing Granites and Problems of Magma Differentiation. Ed. V. S. Koptev-Dvornikov. Moscow, Nedra, 1972.

Shcherbina, V. V. Geochemistry of scandium and Types of Scandium Deposits. *Geology of Rare-element Deposits,* iss. 8. Moscow, Gosgeoltekhizdat, 1966.

PRECIOUS METALS

Precious metals include gold, silver, platinum, and the platinum-group metals – palladium, iridium, rhodium, osmium, and ruthenium. They were named precious because of the ability to preserve their composition and beauty being resistant to tarnish, corrosion and to the most of the chemically active substances.

32 GOLD DEPOSITS

Gold was the first metal known and used by man. Gold articles have been found in the cultural layers of the Neolithic epoch (5-4 thousand years B.C.). Gold was mined in Africa, Asia and south Europe 3-2 thousand years B.C. In Russia, the first gold-quartz lode was discovered in the Urals, in Berezovsk, by a peasant E. Markov in 1745, and the first gold placer was found in the same area by a foreman L. Brusnitsin in 1814. Later gold placers and lodes were discovered in the drainage areas of the Yenisei, Lena, Aldan, Kolyma, and other rivers of Siberia.

Most of the produced gold is hoarded in the form of bars and coins as the national monetary reserves which amount to approximately 40 thousand tons in the capitalist countries. The remaining gold is used to manufacture various articles among which jewelry comes first (50%); the other nonmonetary uses of gold are in the electronics and computer industry and chemistry (35%), and in medicine (10%).

In gold mining and refining, silver, platinum metals, uranium, copper, tungsten, bismuth, tellurium and other elements are extracted. And similarly gold is recovered as a by-product from the refining of copper, zinc, lead, nickel, antimony and other metals. The total amount of the gold recovered as a by-product, however, is 5-7% of its world production.

In the last years the price of gold increased greatly and was about 20 US dollars per gram in 1980.

The world production of gold was 12 thousand tons by and including the 15th century, 760 tons in the 16th century, 900 tons in the 17th century, 1900 tons in the 18th century, 11600 tons in the 19th century, and is assumed to be 80000 tons in the 20th century. So, approximately 110 thousand tons of this metal were extracted from the earth during the world's history. At present, gold is mined in more than 50 countries. In the last ten years the annual production of gold was 800-1200 tons in the capitalist and developing countries.

The gold reserves in the capitalist and developing countries classified as proved with a high degree of assurance are 35 thousand tons; the total resources are estimated at 70 thousand tons.

A unique gold deposit is Witwatersrand in the South African Republic, which is so far the only deposit having the reserves of 25 thousand tons and accounting for 75% of the annual gold production in the western world. The gold content in the primary ores varies from several kilograms to a few grams per ton of ore, and in placers – from a few hundred grams to a few hundred milligrams per cubic metre of sand.

GEOCHEMISTRY
AND MINERALOGY

Gold has fourteen isotopes with mass numbers 192 through 206 and only one stable isotope ^{197}Au. The crustal abundance of gold is $4.5 \cdot 10^{-7}\%$ (4.5 mg/t). The abundances vary as follows (in $1 \cdot 10^{-7}\%$): sea water – 0.4, sedimentary rocks – 1, metamorphic rocks – 0.7 to 4.2, acidic igneous rocks – 2, basic igneous rocks – 2 to 10. The concentration factor of gold is high, averaging 2 000.

The comparatively high gold content in the mantle rocks of a basalt series suggests its supply from the subcrustal stratum of the Earth's outer shells. However, gold occurs in commercial concentrations neither in basalts nor in granite igneous rocks. It is migrated in mobile post-magmatic products most probably in the form of thiosulfite $[Au(S_2O_3)]^{3-}$ and chloride ($AuCl_2^{2-}$ and $AuCl^{2-}$) complex compounds being transported by hydrous solutions forming various hydrothermal deposits (N. Petrovskaya, 1973). Under exogenous conditions gold is freed from the associated endogenous minerals and forms secondary concentrations in iron hats and placers.

The most important commercial mineral in gold deposits is native gold. It contains an admixture of more than 40 accessory elements the most significant of which are silver, platinum metals, copper, iron, lead, bismuth, and antimony. The quality of gold is evaluated by its purity which is determined by the content of gold in 1 000 units of the weight. High-quality gold has a purity of more than 900, and low-quality gold – less than 700. Gold purity in gold deposits is a complex function of the geological and physicochemical factors of mineralization. It increases from young to old deposits, from low-temperature to high-temperature deposits, from shallow to deep-seated deposits, and from primary unaltered to redeposited ores (N. Petrovskaya, 1973).

Gold occurs in ore in the form of irregular inclusions (grains, films, fibres, dendrites), and more rarely in crystals and crystal aggregates. Gold inclusions are classified in size into dispersed (up to 10 μm), small (up to 0.1 mm), medium (up to 1 mm), large (up to 5 mm), and nuggets (more than 5 mm in size or 10 g in weight). The weight of nuggets found in bedrock and placer gold deposits amounts to 36.2 kg (Great Triangle, USSR) and even 285 kg (Holterman's Plate, Australia). Gold is unevenly distributed in bedrock and placer deposits occurring in ore shoots, bonanzas, and leads.

Apart from native gold, 20 gold-bearing minerals are known, which play no significant role in gold production. They include eleven intermetallic compounds – electrum AuAg, küstelite Ag(Au), auricupride Au_2Cu_3, aurostibite $AuSb_2$, rodite Au(Pt, Rh, Ir, Pd) and others, and nine tellurides – calaverite $AuTe_2$, sylvanite (Au, Ag)Te_4, krennerite (Au, Ag)Te_2, petzite Ag_3AuTe_2, and others.

METALLOGENY

The metallogeny of gold is different in the Archean and post-Archean periods of the geological history. In the Archean time gold deposits were formed in relation to subcrustal basalt magma which was responsible for the formation of protogeosynclinal greenstone belts in which gold deposits were localized. In the Proterozoic and later periods a more significant role in the formation of gold deposits belongs to crustal granite magma. In that period gold deposits were formed during geosynclinal and platform cycles, and during the episodes of tectonic and igneous reactivation of platforms.

No gold deposits of large size were formed at the early stage of a geosynclinal cycle in the period of basalt magmatism. Poor gold contents are known from massive sulfide and skarn ores. Hydrothermal gold deposits were formed in some places at the intermediate stage during the main phases of folding and granite batholith emplacement. The majority of post-magmatic, mainly hydrothermal gold deposits appeared at the late stage of a geosynclinal cycle. They were related to two igneous rock assemblages. Plutonogenic hydrothermal gold deposits were associated with small hypabyssal intrusions, and volcanogenic hydrothermal

gold-silver deposits-with an andesite-rhyolite assemblage.

During the platform cycle metamorphogenic deposits were formed in the lower structural level, and secondary gold concentrations in oxidized zones of primary ores and placers – in the upper level.

Hydrothermal gold deposits were also formed during the episodes of intense tectonic and igneous reactivation accompanied by the emplacement of platform granites.

Four main epochs are recognized in the geological history of formation of gold deposits in the Earth. Large gold deposits of greenstone belts were formed in the oldest Archean epoch (3.5-2.5 b. y.). These are known in Canada, South Africa, India, and West Australia. The largest stratiform deposits including the phenomenal auriferous conglomerates of Witwatersrand (South African Republic) were formed in the Proterozoic epoch (2.2-1.8 b. y.). Mainly numerous deposits of gold ore of plutonogenic hydrothermal origin appeared in the Late Paleozoic epoch (300-200 m. y.) which corresponds to the close of the Hercynian cycle. Along with these, volcanogenic hydrothermal deposits including gold-silver ones were widely developed in the Meso-Cenozoic epoch corresponding to the Alpine cycle.

TYPES OF COMMERCIAL DEPOSITS

Commercial gold deposits can be grouped as follows: (1) skarn; (2) plutonogenic hydrothermal; (3) volcanogenic hydrothermal; (4) metamorphogenic; (5) placers.

SKARN DEPOSITS

Skarn gold deposits are rare. They are known in the USSR (Siberia, Tien Shan, Gornyi Altai), in the USA (Cable, Elkhorn, Ouray), in Canada (Nickel Plate), in Mexico (Santa Fe), in Korean People's Democratic Republic (Kholten, Suain), and in other countries. They are normally represented by ordinary limestone skarn of garnet-pyroxene composition which were subject to alteration (hydration) accompanied by the
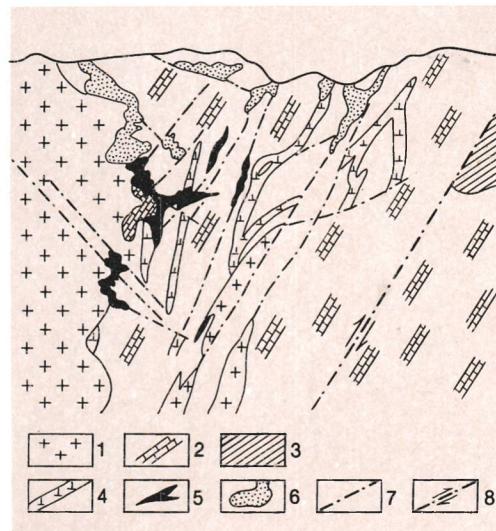
Fig. 111. Schematic section across the central part of the Olkhovskii deposit. [After A. Khazagarov (M. Borodayevskaya, I. Rozhkov, 1974)]:

1 – granite, granodiorite;
2 – limestone, dolomite;
3 – slate, hornfels;
4 – ancient dike;
5 – ore body;
6 – oxidized ore;
7 – fault;
8 – direction of movement along faults

deposition of sulfides including gold-bearing ones.

OLKHOVSKII. The deposit is situated in West Siberia. It is composed of Lower and Middle Cambrian carbonate and sandy-tuffaceous rocks deformed into large folds and broken by faults. The rocks are intruded by granites of Ordovician age, and by diabase, diorite-porphyrite, quartz porphyry and aplite dikes.

At the northern cliff of the granite massif, the carbonate rocks are converted to garnet-pyroxene skarns in which gold-bearing sulfide mineralization is developed (Fig. 111). The ore bodies occur as lenses, pipes and veins complicated by apophyses. Quartz-sulfide veins and stockworks occur in granites and near-contact hornfels. According to D. Timofeevskii, the history of mineral deposition consisted of five stages: (1) skarn; (2) pyrrhotite; (3) quartz-pyrite; (4) polymetallic minerals; and (5) carbonate. Gold is mainly associated with the minerals of the polymetallic stage during which
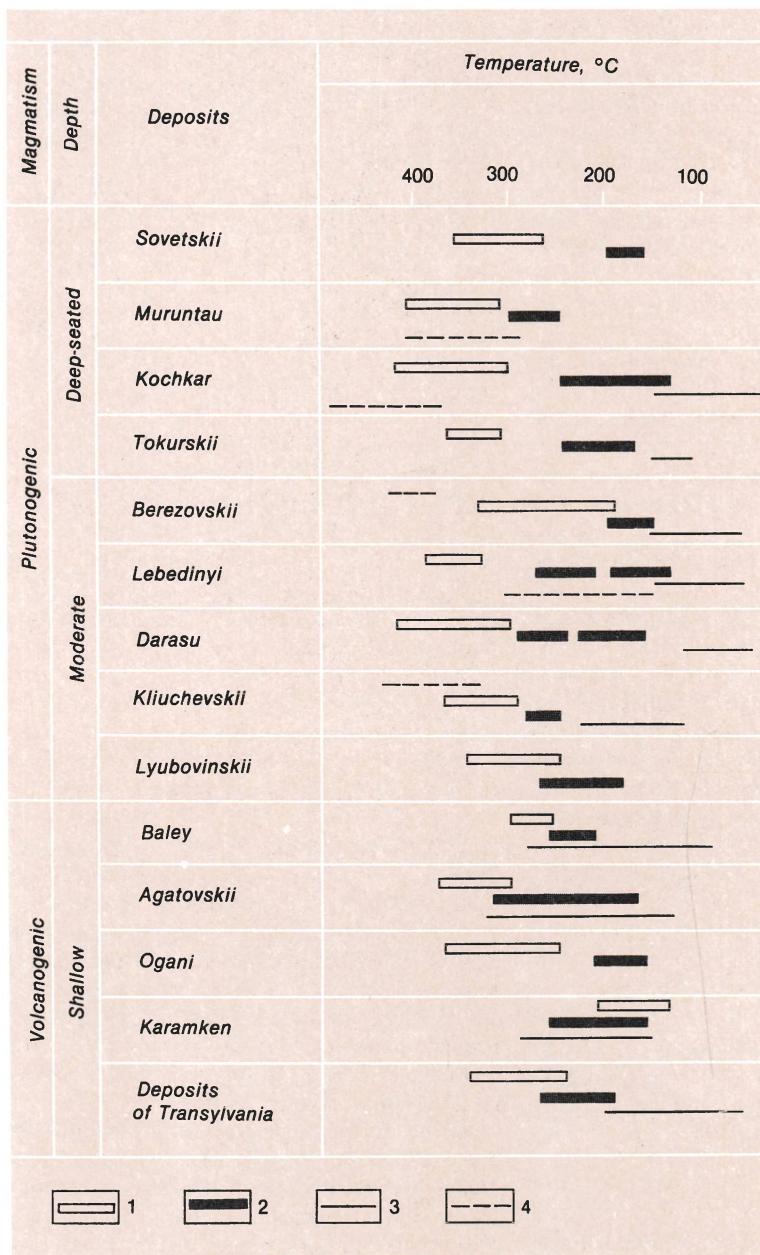
Fig. 112. Temperatures of mineral deposition in hydrothermal gold deposits. [After N. Petrovskaya (1973) with some additions]:
1 — early stages;
2 — main productive stages;
3 — late stages;
4 — stages of mineralization during which no gold ores were deposited

chalcopyrite, sphalerite, galena, grey ores, bismuthine, gold and silver tellurides were deposited. The wall-rock alteration is manifested in the beresitization of acidic rocks, chloritization and sericitization of basic rocks, and slight serpentinization of limestones. This is a medium-depth and moderate-temperature deposit.

HYDROTHERMAL DEPOSITS

Hydrothermal gold deposits are most widespread. N. Petrovskaya (1973), M. Borodayevskaya and I. Rozhkov (1978) attach paramount importance in the classification of these deposits to their depth of formation. They propose to classify them

into deep-seated (5-10 km and more), medium (5-1.5 km), and shallow or near-surface deposits (less than 1.5 km). All hydrothermal gold deposits are multiphase ones. The early phases are usually poor in gold content; the intermediate phases are most enriched in gold, they are referred to by N. Petrovskaya as productive phases; and the late phases are of low value as regards gold concentration. Attempts to subdivide hydrothermal gold deposits on the basis of the temperature of formation had no success in view of the fact that productive phases in most of the deposits fall within the same temperature range – 250-150° (Fig. 112).

In this book hydrothermal deposits are divided into plutonogenic and volcanogenic ones which are essentially different in conditions of formation, occurrence, and ore composition. The ore formations in hydrothermal gold deposits are: gold-quartz, gold-sulfide, gold-quartz-sulfide, gold-quartz-chalcedony-sulfide, gold-silver-quartz-adular, gold-quartz-arsenopyrite, gold-quartz-antimonite, gold-quartz-bismuthine, gold-barite, and gold-carbonate. The most representative plutonogenic hydrothermal deposits belong to relatively simple and unmarkedly different gold-quartz and gold-quartz-sulfide formations. They are characterized by beresitization and listvenitization of ore-enclosing rocks. Volcanogenic hydrothermal deposits are distinguished by more complex formations such as gold-quartz-chalcedony-sulfide, gold-silver-quartz-adular, and gold-sulfide (massive sulfide). The wall rocks are usually propylitized, alunitized and argillized, which indicates the acidic nature of mineralizing solutions.

Plutonogenic Hydrothermal Deposits

Gold deposits of this type are associated with granitoid batholiths of the intermediate stage of a geosynclinal cycle, with small-size hypabyssal intrusions of the later stage, and with some hypabyssal intrusions emplaced during the stage of platform reactivation. Such deposits are widespread in auriferous provinces with geosynclinal and platform granite and alkali-granite magmatism of all metallogenic epochs. The ores are commonly of simple quartz composition, massive and stringer structure, and granular texture.

Deposits of Gold-quartz Formation

MURUNTAU. The deposit is situated in a Paleozoic fold zone of the Tien Shan Mountains. It is composed of a flysch-like sequence of interstratified, thinly bedded sandstones and slates of the Upper Proterozoic to Lower Paleozoic age. Intrusive rocks occur in granodiorite stocks and belts of granite porphyry and syenite porphyry dikes of the Late Paleozoic age. The sedimentary strata are deformed into gentle folds and broken by strike-slip faults. The most important are the Southern, North-eastern, and Structural faults. The faults are accompanied by near-fault folds and fracture zones controlling mineralization. The gold deposit is a stockwork produced by a dense network of steeply and gently dipping joints and tensile and shear fractures (Fig. 113). A number of ore zones containing ore bodies of a complex and irregular shape were outlined within the stockwork by means of sampling.

The predominant mineral in the Muruntau ores is quartz; the minerals other than quartz account for 0.5-1.5%. The gangue minerals are K-feldspar, albite, biotite, tourmaline, and calcite. The most common ore minearls are pyrite and arsenopyrite; scheelite, sphalerite, galena, bismuthine, native bismuth, and sulphosalts of silver were noted in minor amounts.

The process of ore deposition in Muruntau had a long history. According to M. Borodayevskaya and I. Rozhkov (1978), the bulk of reef quartz was deposited at the first phase. The second phase consisted of three stages which include comb-like quartz, pyrite-arsenopyrite and pyrite-tourmaline deposition. The third phase is divided into the stages of rosette quartz and gold-base metal deposition with gold-quartz, base metal and carbonate sub-stages. In the opinion of I. Yudin et al, the Muruntau ores were formed at the first stage at temperatures of 360-160 °C, at the second stage – at 360-120 °C, and at the third
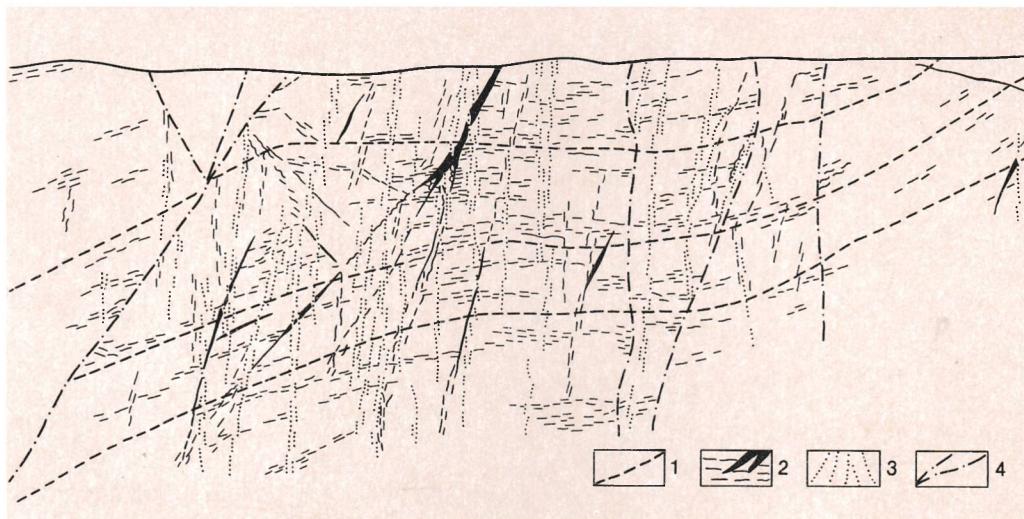
Fig. 113. The Muruntau ore stockwork. [After S. Sher (M. Borodayevskaya, I. Rozhkov, 1974)]:

1 — boundaries of lithologic units with different proportions of phyllite-like slates and aleurolites;
2 — quartz veins and veinlets;

3 — quartz-sulfide veinlets;
4 — faults

stage – at 420-100 °C. The enclosing rocks underwent contact metamorphism and hydrothermal-metasomatic alteration. Contact metamorphism created a broad aureole of biotite and amphibole hornfels; and hydrothermal alteration produced wall-rock quartz and quartz-microcline metasomatites. BENDIGO. The deposit is situated in Victoria, Australia. The rocks of the goldfield consist of Lower Ordovician sandstones and slates with rare interbeds of calcareous rocks. The rocks are deformed into a system of dense folds complicated by bedding-plane overthrust and cross faults. Massifs of Late Devonian granites to which the Bendigo mineralization appears to be genetically related occur in the vicinity. The whole complex of the rocks, tectonic structures and gold-bearing quartz reefs is cut by monchiquite dikes of Tertiary age.

Within the district of 25 by 5 km in area, thirteen sub-parallel ore-productive anticlines were outlined; their axial planes are spaced 200 to 400 m apart. The ore bodies occur in the crests of the anticlines in the form of saddle reefs with branching apophyses or spurs; there are also bed-shaped reefs and fault reefs that cut across the bedding (Fig. 114). The reefs are often repeated downward forming a tier and their number in the vertical section of the ore-producing anticlines down to a depth of 1 400 m, mined with the shafts, sometimes amounts up to 24. The reefs extend several kilometres in length with a width of 7 to 15 m; their thickness reaches 10 m at the crests and rapidly contracts at the limbs of the anticlines.

The ore consists of gold-bearing quartz; minor amounts of albite, ankerite, sericite and carbonates are present. The content of sulfides does not exceed 1-2%. The most important of them are arsenopyrite, pyrite, pyrrhotite, galena, sphalerite, and antimonite. Coarse-grained gold occurs in quartz; some minor quantity of fine-grained gold is associated with the sulfides. No marked alteration of the wall rocks has been observed. Approximately 600 tons of gold have been recovered from the Bendigo goldfield which has been worked out to a significant extent; the gold content in the ore is 5 to 25 ppm. A few dozens of tons of gold have been mined from placer deposits.

Deposits of
Gold-quartz-sulfide Formation

BEREZOVSKII. The deposit is situated in the Urals, USSR. The rocks of the goldfield consist of Middle and Lower Paleozoic
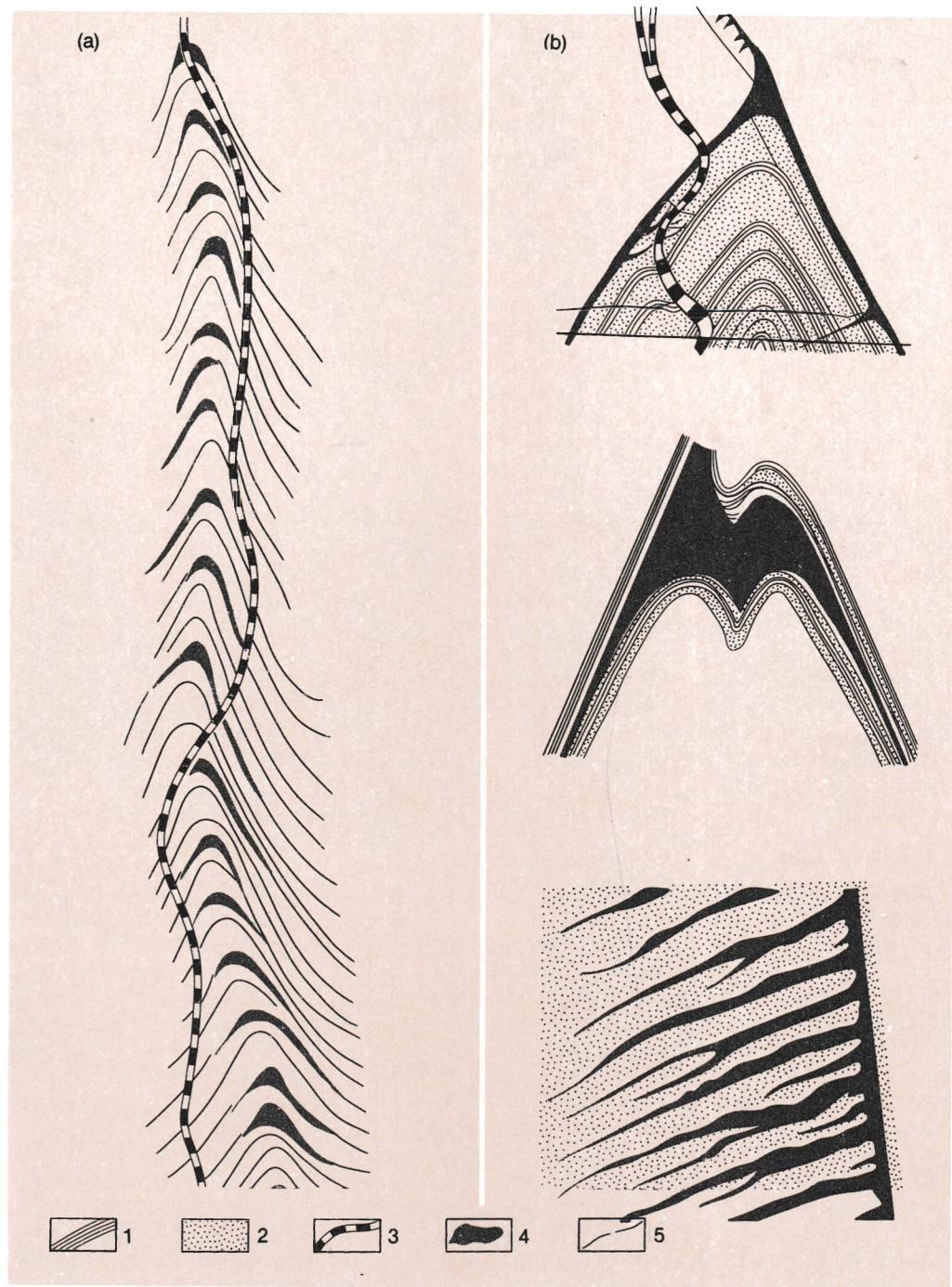
Fig. 114. Sections across a vein system (*a*) and across separate veins (*b*) of the Bendigo gold deposit. (After D. Thomas):

1 – shales;
2 – sandstones;
3 – monchiquite dikes;

4 – ore bodies;
5 – faults

sandstones, slates and tuffites with interstratified bed-like bodies of serpentinized peridotites and pyroxenites. The complex of stratified rocks forms a gentle syncline broken by faults and cut by dikes which, as N. and M. Borodayevskii point out, occur in the following succession: plagiosyenite-porphyry, lamprophyre, granodiorite-porphyry, granite-porphyry, and plagiogranite-porphyry. Dikes are implaced in several belts spaced 80 to 100 m apart. The distance between dikes varies within 5-10 m; they are several metres in width.

Gold mineralization is concentrated within the dike belts in two groups of quartz and quartz-sulfide reefs. One of them known as the "ladder" or "banded" consists of en echelon reefs cutting across the dikes from one contact to the other. The reefs of the second group called "Krasichnyi" reefs extend beyond the dikes into the enclosing rocks (Fig. 115). Localization of the gold-bearing reefs in the dike fissures was conditioned by cracking of the dikes during tectonic deformations as friable plates lying in plastic volcanic and sedimentary rocks. The goldfield is distinguished by an abundance of small-size reefs.

The reefs are composed of coarse-grained quartz with abundant pyrite, and of other minerals such as tourmaline, ankerite, dolomite, calcite, scheelite, chalcopyrite, galena, tetrahedrite, and aikinite. Gold occurs both in quartz and in a fine dispersed state in sulfides. P. Kutyukhin thinks that mineral deposition occurred in four stages: quartz, quartz-pyrite, tetrahedrite-galena-aikinite, and carbonate. The ore-bearing granitoid dikes are altered into an aggregate of quartz, sericite and pyrite, which was named by A. Karpinskii "beresite" and is known by this name in literature. The ore-enclosing serpentinites are converted into listvenites.

According to the data of L. Koltun, the temperature of early quartz crystallization was $420\text{-}370\,^{\circ}C$, that of the quartz-pyrite stage $-320\text{-}170\,^{\circ}C$, of the productive polymetallic stage $-160\text{-}120\,^{\circ}C$, and the temperature of the final stage of ore deposition was $120\text{-}60\,^{\circ}C$.

DARASUN. The deposit is located within a belt of Mesozoic reactivation of a Paleo-
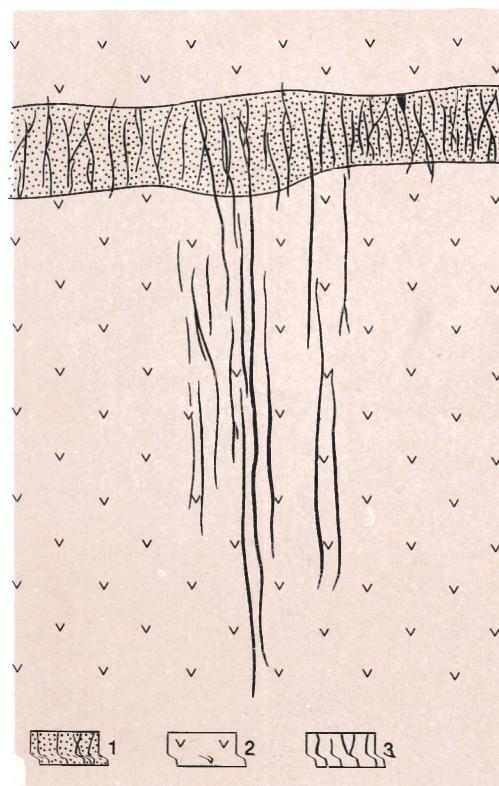
Fig. 115. A fragment of the Berezovskii gold deposit. [After M. and N. Borodayevskii (1974)]:

1 – beresitized granite porphyry dike with ladder reefs;
2 – serpentines;
3 – Krasichnyi reefs

zoic fold area in Siberia. The area of the goldfield is composed of Lower Paleozoic gabbroids and amphibolites, Middle Paleozoic granodiorites, and Upper Paleozoic granites and syenites. The district contains numerous dikes of melanocratic rocks. The Paleozoic strata are intruded by stocks of Mesozoic plagiogranite-porphyries with which the mineralization is genetically associated.

Numerous quartz-sulfide reefs are controlled by a system of intersecting shear fractures of a north-eastern and north-western strike. In the opinion of T. Timofeevskii there were seven stages of mineral deposition: (1) quartz-tourmaline (quartz, tourmaline, chlorite, and to a lesser extent pyrite, muscovite, epidote, rutile, and wolframite); (2) quartz-pyrite; (3) pyrite-arsenopyrite with sphalerite; (4) galena-
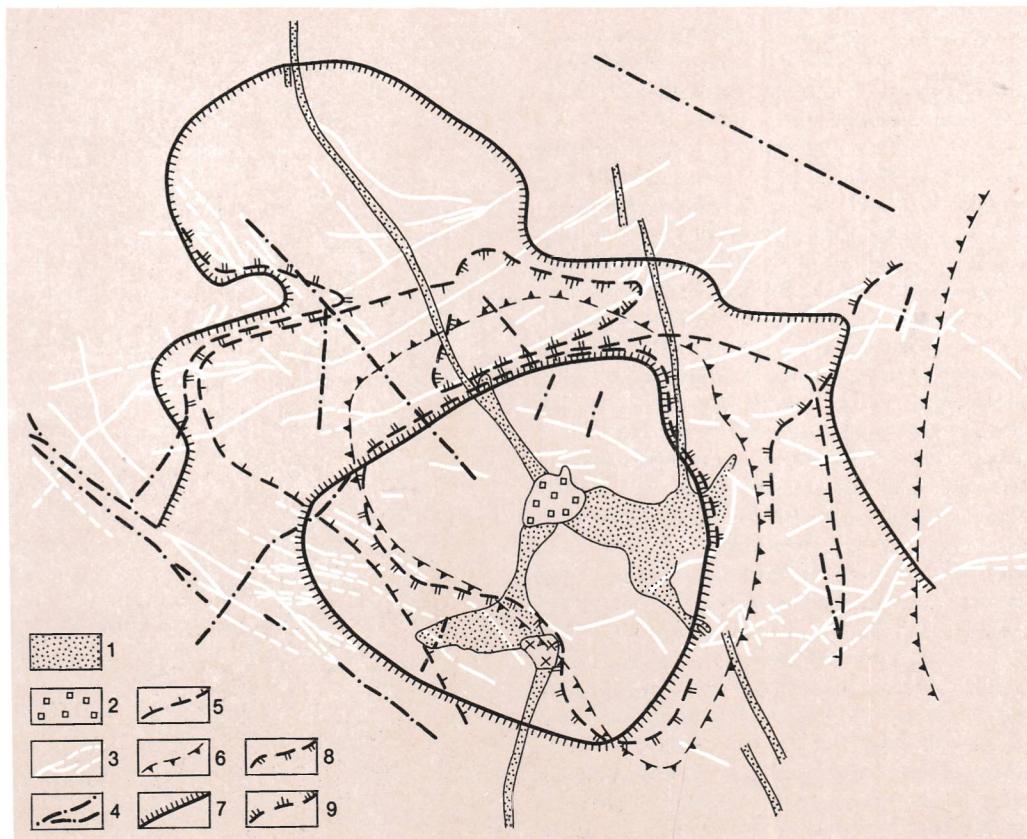
Fig. 116. A schematic map of the zonal distribution of mineral assemblages at the Darasun gold deposit. [After D. Timofeevskii (M. Borodayevskaya, I. Rozhkov, 1974)].

1 – plagiogranite-porphyry;
2 – explosive breccia;
3 – gold-bearing quartz-sulfide veins;
4 – faults;
5-9 – boundaries of mineral assemblages:
5 – quartz-tourmaline;

6 – pyrite-arsenopyrite;
7 – galena-sphalerite;
8 – bournonite-tetrahedrite-chalcopyrite;
9 – sulphoantimonite. Dash signs on the contour lines are directed towards the development of mineral assemblages

sphalerite (galena, sphalerite, chalcopyrite, grey ore, cubanite and bournonite); (5) pyrrhotite-tetrahedrite-chalcopyrite (with bismuth, silver, gold, copper, lead, and electrum tellurides); (6) quartz-sulphoantimonite (lead sulphoantimonites, antimonite, berthierite, and cleiophane); (7) carbonate (calcite, dolomite, ankerite, chalcedony, barite, gypsum, and marcasite).

The hydrothermal alteration of the wall rocks is manifested in beresitization of acidic rocks and listvenitization of basic rocks.

The successively deposited mineral assemblages are concentrically localized around the stocks of plagiogranite-porphyries and the associated explosive brec-

cias (Fig. 116). The localization of mineral products of the successive stages of deposition in intermittently opened ore-enclosing fissures resulted in the uneven distribution of minerals. Some of them are characterized by simple mineral assemblages produced at a lesser number of deposition stages, while others are compositionally complex consisting of different mineral associations which represent the majority of stages.

As reported by M. Sakharova, the ores become compositionally simple with depth in all the reefs, and the amount of sulfides decreases because they are replaced by quartz.

The mineral deposition occurred in the

temperature range of 400-275 °C at the early stages, at 300-170 °C – at the intermediate, most productive stages, and at 130-50 °C – at the final stage.

KOLAR. The deposit is situated in the Mysore Plateau, India. The goldfield is located in a narrow trough of a north-south trend extending for 70-75 km and having a width of 3-5 km. The trough is filled with Archean gneisses, and the gold-bearing ores are confined to essentially amphibole rocks located within gneissic rocks. These ancient crystaline rocks occur as a steeply dipping monocline of an intense gneissic structure complicated by folding along the strike and down the dip. There are outcrops of Archean granites in the north and south. Series of gold-bearing reefs concordant with gneisses and amphibolites and repeating their bends to which the swollen parts of ore bodies are confined occur within the deposit having 25 by 1 km in area (Fig. 117). The reefs constitute the belts consisting of en echelon lenses, veins and veinlets. The ore zones are up to 8 km in length, and 0.5 to 15 m (average 1.5 m) in width with the thickness of individual ore bodies ranging from 2 cm to 1.2 m (occasionally reaching 3 m). The ore bodies are being mined to a depth of 3 500 m.

As regards the mineral composition, there are two types of lodes in the deposit, gold-quartz and gold-quartz-sulfide lodes. The gold-quartz lodes are made up of shattered quartz with sulfides and other minerals, the total amount of which is not more than 1%. The principal minerals are pyrrhotite, pyrite, arsenopyrite, galena, hessite, altaite, scheelite, magnetite, and ilmenite. The average gold content is 10-15 ppm. The gold-quartz-sulfide lodes are made up of quartz and sulfides, the sulfides composing 10-15% of the lode material. They include pyrrhotite, arsenopyrite, pyrite, chalcopyrite, and galena. The average gold content is 4-6 ppm.

The wall-rock alteration of amphibolites has a zonal pattern: a thin diopside rim at the contact with the gold-quartz lodes is succeeded by a rim of hornblende with epidote which is followed outward by a broad aureole of quartz-biotite schists. Approximately 700 tons of gold have been recovered from the Kolar goldfield.
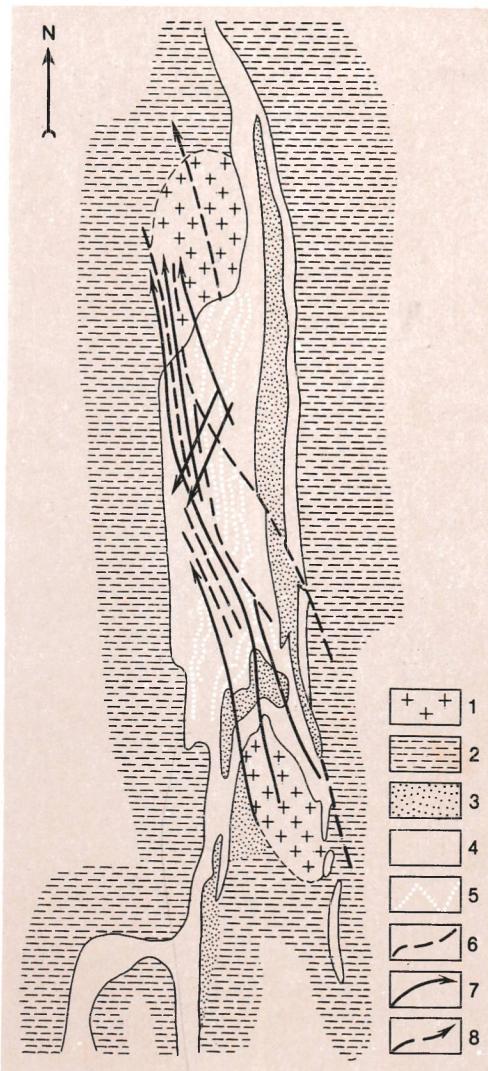
Fig. 117. Geological structure of the Kolar gold deposit. (After S. Narayanaswami):
1–granites;
2–Peninsular gneisses;
3–Champion gneisses;
4–Kolar schist belt;
5–gold-bearing bodies;
6–faults;
7–axes of en echelon superimposed folds;
8–axes of primary synclinal folds

Volcanogenic Hydrothermal Deposits

The gold deposits of this type can be divided into two groups. One group belongs to Archean ophiolite belts occurring within platform areas, and the other – to
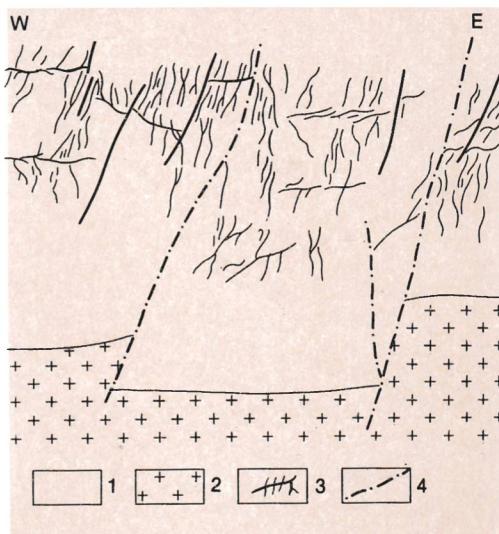
Fig. 118. A fragment of the section across the Baley gold deposit. [After P. Bernshtein (M. Borodayevskaya, I. Rozhkov, 1974)]:

1–Cretaceous conglomerates;
2–granodiorites;
3–gold-bearing veins;
4–faults

late-geosynclinal andesite-rhyolite belts the most pronounced of which are the ore-bearing areas of the circum-Pacific belt and the inner arc of the Carpathians. These deposits are characterized by complex ore compositions, eutaxitic and colloform ore textures, intense acidic alteration of the wall rocks ranging from tourmalinization to alunitization, irregular bonanza gold concentration frequently together with silver, and a relatively short vertical range of mineralization.

Deposits of Gold-quartz-chalcedony-sulfide Formation

BALEY. This deposit and the similar Taseevskii deposit south of it are situated in the Transbaikal region in an area of completed Paleozoic folding, which was reactivated in the Late Mesozoic time. It is located in a graben of early Cretaceous origin. The graben has a basement of Paleozoic granites and Upper Jurassic conglomerates, and is filled with Upper Cretaceous and Tertiary continental terrigenous sediments reaching 650 m in thickness. The sedimentary rocks include

small diorite-porphyry bodies and dikes, explosive breccias, and silicified tuffs, which were classified by N. Fogelman as products of early Cretaceous volcanism, and whose sources were responsible for the Baley mineralization.

The Baley deposit is located at the northern side of the graben where a system of sublatitudinal steep and gently dipping fissures filled with gold ore extend along the fault bordering the graben (Fig. 118). The fissures of this system extend into the granites of the Udinskii massif adjacent to the graben and into the conglomerates, sandstones, and slates lying within the graben. The ore occurs in stockworks, linear lode zones and separate lodes accompanied by aureoles of disseminated mineralization. Within these zones commercial ores form shoots which are localized beneath flat-lying crush and silicified zones which act as screens.

Quartz and chalcedony make up 95% of the Baley ores. N. Petrovskaya recognized six stages of ore deposition: (1) quartz-chalcedony; (2) quartz-adular-kaolinite; (3) quartz-carbonate; (4) quartz-sulfide (pyrite, marcasite, arsenopyrite, chalcopyrite, sphalerite, galena, and linneite); (5) gold-pyrargyrite; and (6) quartz-antimonite.

The hydrothermal alteration of the wall rocks began with sericitization which was succeeded by silicification and later was followed by adularization, kaolinization and carbonatization, i.e. by the processes which are most closely related to gold precipitation.

According to Yu. Lyakhov, the Baley ores were formed at a temperature of 270-150 °C, at a pressure of 40-30 kgf/cm^2, and at a depth of 200-150 m.

ZOD. The deposit is located in the Upper Cretaceous ophiolite belt of the Small Caucasus. It is a mineralized crush zone of a west-east trend which is cutting across and deforming peridotites and gabbros, and tuff rocks enclosing them. Mineralization is localized in quartz-chalcedony-carbonate veins and stringers consisting of abundant sulfides and other ore minerals (Fig. 119). The essential minerals are pyrrhotite, pyrite, marcasite, arsenopyrite, chalcopyrite, sphalerite, grey ore, freibergite, antimonite,
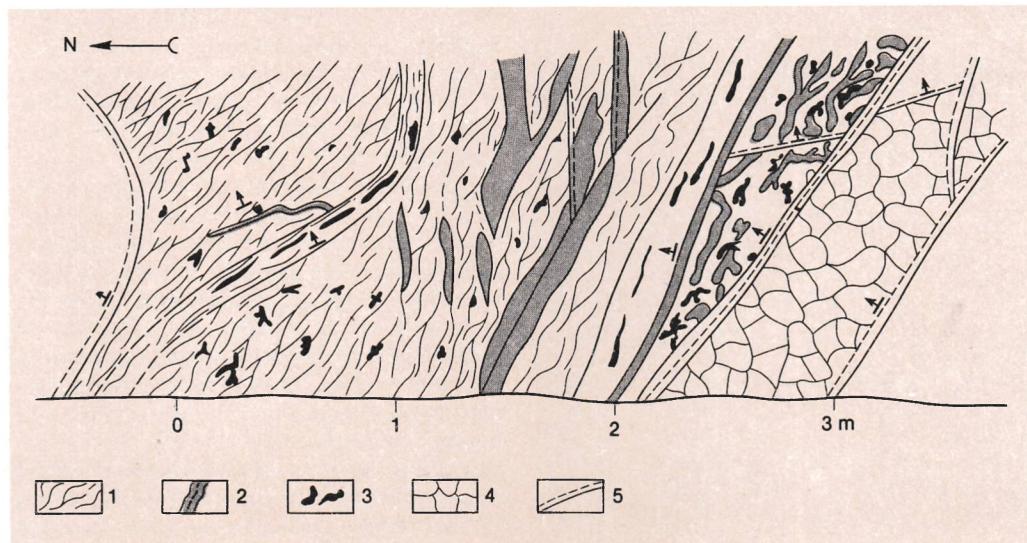
Fig. 119. Section across the ore zone of the Zod gold deposit. [After M. Konstantinov (M. Borodayevskaya, I. Rozhkov, 1974)]:

1–crushed zone;
2–quartz veinlets;
3–gold-sulfide dissemination;

4–breccia;
5–fractures with clay gouge

and less common sulphosalts, tellurides, arsenides, and other more rare minerals.

The history of ore deposition in this deposit was divided by M. Konstantinov into five stages: (1) quartz-chalcedony-sericite-pyrite; (2) quartz-breunnerite-pyrite-arsenopyrite (first productive stage); (3) quartz-marcasite-arsenopyrite-sulphoantimonite-telluride (second productive stage); (4) quartz-antimonite; and (5) quartz-carbonate.

Intense hydrothermal metasomatism is manifested in the transformation of the basic rocks of the mineralized zone of the Zod deposit into an aggregate of quartz-carbonate-talc composition.

CRIPPLE CREEK. The deposit is situated in Colorado, the USA. It is associated with a centre of volcanic activity occurring in a field of Precambrian granites. The volcanic centre was formed in an area which is at present a graben-shape depression filled with conglomerates, sandstones and siltstones at the base, and tuffs reaching 900 m in thickness at the top. The tuffs are cut by phonolite, syenite and basalt dikes. The volcanic process terminated in the formation of a basalt crater and an accompanying system of fissures of a north-western and north-eastern trend.

Three types of ore bodies are known within the Cripple Creek goldfield which is 6.5 by 3.2 km in area: (1) veins filling the above mentioned fissures reaching 1.5 km in length and 0.6 m in width and mined to a depth of 900 m; (2) ore bodies of irregular shape commonly found at the intersections of fissures; and (3) ore pipes composed of mineralized explosive breccia of the "Cresson bonanza" type reaching 100 m in diametre (Fig. 120).

Three stages can be distinguished in the history of the Cripple Creek ore deposition: (1) alteration of the host rocks with newly formed hydrothermal quartz, adular, fluorite, and pyrite; (2) vein quartz-fluorite-pyrite with dolomite, ankerite, sphalerite, galena, tetrahedrite, tellurides, and celestite; and (3) quartz-chalcedony with marcasite and cinnabar.

600 tons of gold have been mined from the Cripple Creek deposit with the average gold content of 10-12 ppm.
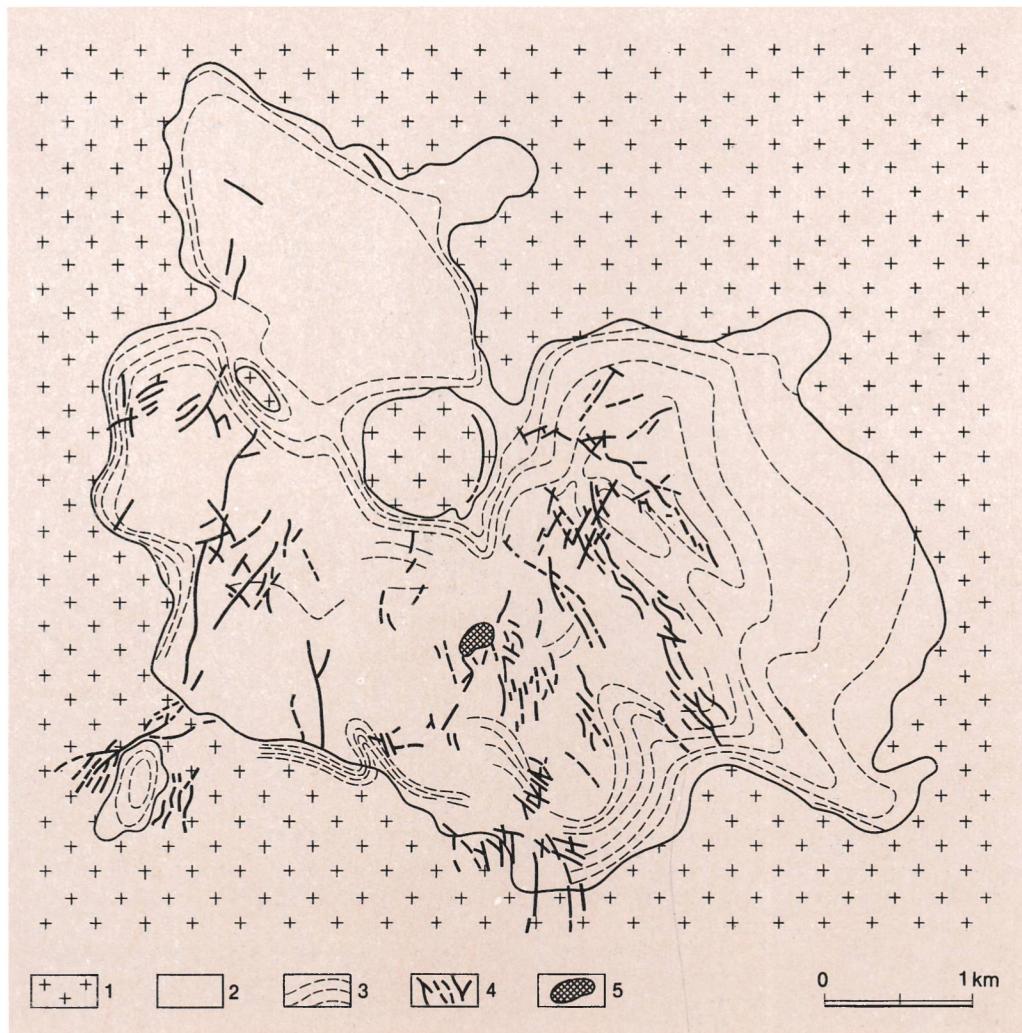
Fig. 120. Geological structure of the Cripple Creek gold deposit. (After G. Loughlin and A. Koschmann):

1—Precambrian granites;
2—Tertiary volcanogenic rocks;
3—isohypses of the walls of a volcano-tectonic structure (interval of 150 m);

4—principal gold-quartz veins;
5—body of gold-bearing breccia (Cresson bonanza)

Deposits of Gold-silver-quartz-adular Formation

KARAMKEN. The deposit is located within the Okhotsk-Chukotka volcanic belt and is associated with a volcano of Late Cretaceous age. It is localized in a volcanic depression, probably in a caldera, filled with sedimentary, volcanic and plutonic rocks. The base of the sequence is a Lower Cretaceous series of conglomerates, sandstones and siltstones 400 m in thickness.

Above follow Upper Cretaceous basalt, andesite, dacite, and rhyolite flows and their ignimbrites and tuffs totalling 500 to 1 000 m in thickness. The stratified sedimentary and extrusive rocks are flat-lying. They are intruded by hypabyssal diorite-porphyries, subvolcanic andesites and rhyolites, and by post-mineralization basalt and andesite dikes. The structure of the deposit is controlled by a system of faults which break the area into blocks. The major fault of

Fig. 121. A vein cluster in the Karamken gold deposit. (M. Borodayevskaya, I. Rozhkov, 1974):

1–hydrothermally altered andesites;
2–veins of the adular (productive) stage;
3–veins of the second quartz-carbonate stage;

4–veins of the third quartz-carbonate stage;
5–intraore faults;
6–post-ore faults

a north-western strike is accompanied by fractures of a more or less west-east and north-south direction. Besides, arcuate and radial fractures of earlier origin are present. The ore bodies are veins and vein clusters filling the faults and fractures (Fig. 121).

The veins are predominantly made up of quartz (60-70%) and adular (5-40%); less common are carbonates, and more rare are hydromica, chlorite, and kaolinite. Ore minerals (0.5-1.5%) occur as dotted lines of fine inclusions extending along colloform quartz-adular bands.

Mineral deposition in Karamken occurred during a long process of concentration of quartz together with carbonates, pyrite, and some other minerals; the process was interrupted by the deposition of adular and the accompanying ore mineralization. According to A. Nekrasova, mineralization occurred in five stages: (1) quartz-pyrite; (2) early quartz-carbonate (sphalerite, galena); (3) adular (hydromica, chlorite, kaolinite, barite, pyrite, marcasite, sulphostannates, grey ore, silver sulphosalts, selenides, gold, and silver); intermediate quartz-carbonate (chlorite, zeolites, grey ore, cinnabar, and antimonite); (5) late quartz-carbonate. The temperature at the early stages of ore formation was 400-70 °C, at the productive stage – 256-75 °C, and at the late stages – 300-75 °C.
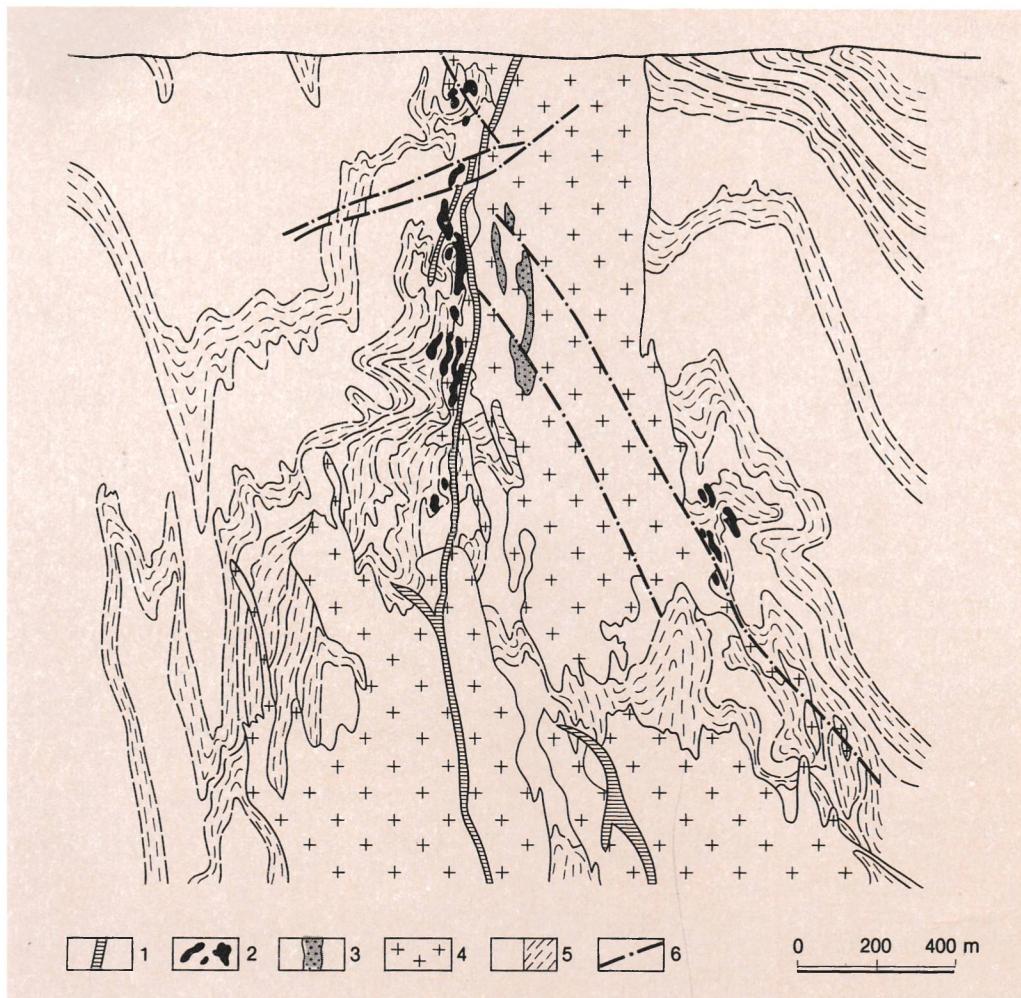
Fig. 122. Geological section across the Porcupine deposit. (After A. Griffiths).

1–diabase dikes;
2–gold-bearing ore bodies;
3–copper ore;
4–porphyry;

5–greenstone basic volcanic rocks:
   (a) massive;
   (b) layered;
6–faults

The zonality of the Karamken ore bodies, according to A. Nekrasova, is manifested in development of a canfieldite-freibergite-chalcopyrite ore association at the top, pyrite-sphalerite in the middle, and a canfieldite association in the deep parts of the ore bodies.

The ore-bearing rocks underwent intense hydrothermal alteration. The altered rocks thus produced are of propylite, quartz-hydromica, quartz-adular, quartz-kaolinite, and quartz-alunite facies.

PORCUPINE. The deposit is situated in the Keewatin province in the south of Canada (S. Sher, 1972). It is an ancient deposit localized in the Archean ophiolite belt of the Canadian Schield. The goldfield is composed of metamorphosed diabases intruded by porphyries. The greenstone-altered diabases form massive and layered varieties of pillow structure. Dunites and peridotites altered to serpentinite-talc-chlorite schists are present. The ore-bearing volcanic strata are folded into complex, intensely corrugated folds broken by faults with a small amplitude of displacement (Fig. 122).

The ore bodies are represented by irregular groups of festooned veins and zones of veinlets. Most of the ore bodies extend for 300 m along the strike and dip. They range in width from 1 m to 25 m, with an average of about 3 m. Where one ore zone wedges out, the next zone forming en echelon appears. The ore bodies within the goldfield, having 24 km by 13 km in size, have been worked out to a depth of 1 500 m.

The principal gangue minerals of the ore bodies are: quartz, ankerite, and albite which replaces potassic feldspar commonly found in the ores of the considered formation. Anhydrite grading into gypsum is present at depth.

According to E. Keays and A. Griffiths, the Porcupine ores were deposited in five stages: (1) ankerite (with tourmaline and scheelite) (2) albite-pyrite; (3) carbonate-pyrite (with arsenopyrite); (4) quartz (pyrrhotite, chalcopyrite, sphalerite, galena, tennantite, gold and silver tellurides); (5) quartz-carbonate calcite, rhodochrosite). Gold was deposited at two stages: in the finely dispersed state it precipitated with early pyrite, and in more coarse particles – at the fourth stage, mainly in quartz.

The gold-bearing veins in basic volcanic rocks are more abundant in gold (10-12 ppm) than those occurring in porphyries (2-3 ppm). The gold/silver ratio is 4.5 : 1. The hydrothermal alteration of host rocks are manifested in carbonatization, silicification, chloritization and formation of talc, and pyrite.

The Porcupine goldfield has produced more than 1 500 tons of gold.

Deposits
of Gold-sulfide Formation

This formation includes gold-bearing massive-sulfide deposits occurring in basalt-like volcanic complexes of the early stage of a geosynclinal cycle. The gold content of the primary ores is usually too low to mine them economically as independent gold targets. Gold and silver contained in them are extracted as by-products in the recovery of copper, lead and zinc. For this reason the deposits of this type are not described here. It is necessary, however, to note that the zones of oxidized
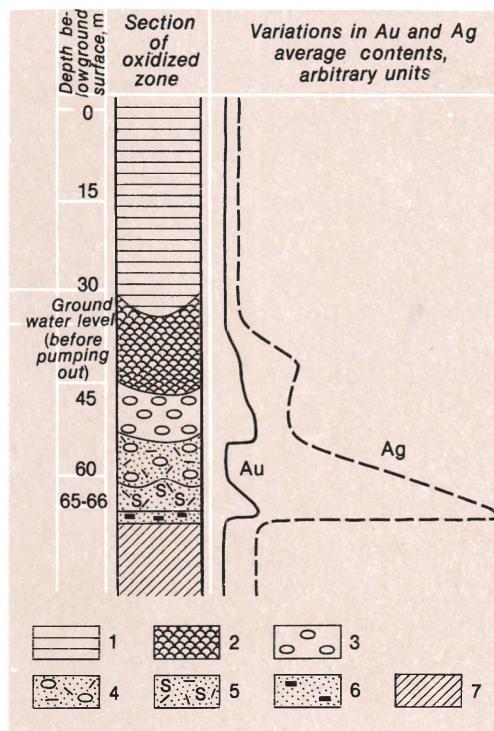
Fig. 123. Localization of gold and silver in the oxidized zone of massive sulfide ore in the Maykain gold deposit. [After V. Kreiter (M. Borodayevskaya, I. Rozhkov, 1974)]:
1–clay;
2–brown iron ore;
3–jarosite;
4–quartz-barite fine-grained sand with jarosite;
5–same with sulphur;
6–fine-grained sand with pyrite;
7–massive sulfide ore

ores in massive sulfide deposits may contain secondary gold and silver concentrations of economic value.

MAYKAIN. The primary ore of this massive-sulfide deposit located in the north of Kazakhstan, the USSR, contains 80% pyrite. and chalcopyrite, galena, grey ore, quartz. and barite. The zone of oxidized ores extends to a depth of 70 m. According to V. Kreiter, it has the following zonal succession (downward):

(1) "iron hat" consisting of clay to a depth of 20-35 m, and brown iron ore up to 40-45 m;

(2) jarosite up to 50-55 m;

(3) loose, fine-grained sand of quartz-
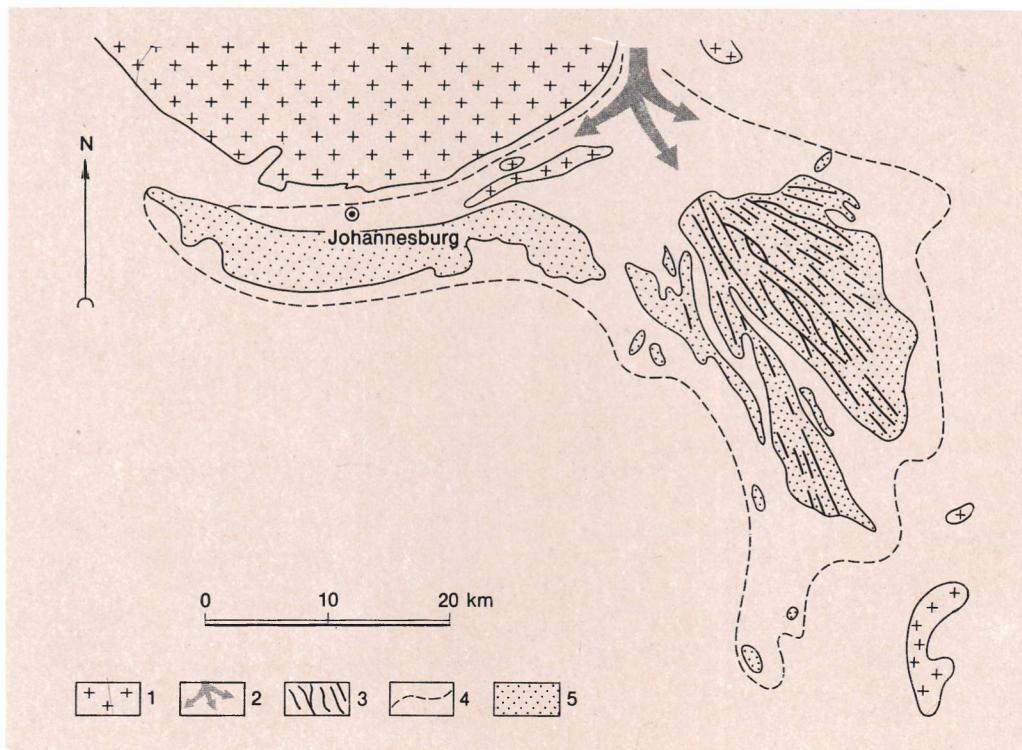
Fig. 124. The Witwatersrand fan-like basin. (After D. Pretorius):
1—basement granites;
2—direction of gold-bearing material inflow;
3—Au-rich leads in ancient streams;
4—outline of Leader reef;
5—worked-out area within the reef limits

barite composition with jarosite up to 60-62 m, and with native sulphur up to 64-66 m; (4) fine-grained massive-sulfide sand up to 66.5-67.5 m.

Gold and silver are represented by secondary minerals, gold is present in fine films, and silver in silver halides. They are unevenly distributed in the column of the oxidized ores being most concentrated in the lower part where the gold and silver content is 7 to 10 times as high as that of the primary sulfide ore (Fig. 123).

METAMORPHOGENIC DEPOSITS

This category of gold deposits comprises two groups: metamorphosed deposits consisting of ancient auriferous conglomerates, and metamorphic deposits composed of ancient gold-bearing black shales.

Metamorphosed Auriferous Conglomerates

WITWATERSRAND. This unique gold deposit is situated in the South African Republic, south of Johannesburg extending 350 km to the north-east and 200 km to the north-west. Structurally it is a block of Archean rocks which was subject to long subsidence during the Proterozoic compensated by accumulation of a thick sequence of fluvial deltaic deposits, which were covered by continental sediments in the Paleozoic and Cenozoic time. The basement of this sequence consists of Archean granite-gneisses intruded by basic rocks (3 250 m. y.) and granites (3 200-3 050 m. y.).

The Proterozoic deposits are a sequence of embedded and overlapping fluvial-deltaic fans converted into conglomerate, quartzite and slate beds alternating with volcanic sheets (Fig. 124). The section includes four stratigraphic units (upwards): Witwatersrand,
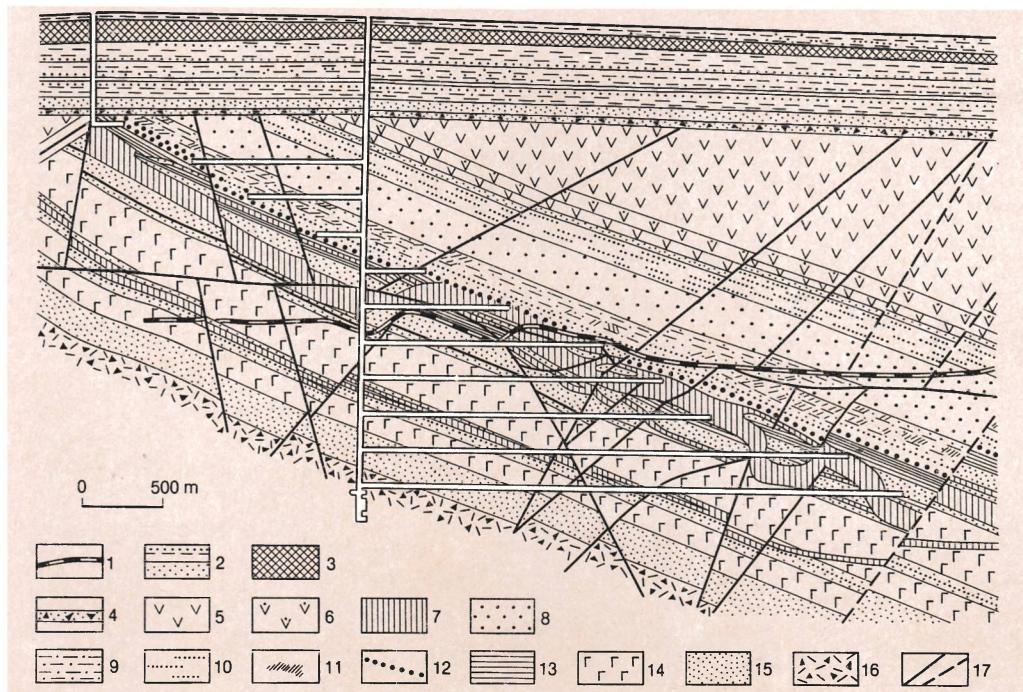
Fig. 125. Auriferous conglomerates of the Leslie-Gold Mine, Witwatersrand. (After K. Tweedle):

Paleozoic:
1 – dolerite dikes;
2 – carbonaceous deposits;
3 – dolerite;
4 – basement rocks;
Proterozoic-Ventersdorp system:
5 – amygdaloidal lavas;
6 – porphyrites and their tuffs;
7 – diabase (sill at the footwall); Witwatersrand system, Kimberley-Elsburg series;

8 – shales;
9 – quartzites;
10 – zone of discontinuous reefs;
11 – zone of quartzites;
12 – Kimberley Reef;
13 – Kimberley shales; Main Bird series:
14 – amygdaloidal lavas;
15 – quartzites;
16 – blue gravel-stones;
17 – faults

stratigraphic units (upwards): Witwatersrand, Ventersdorp, Transvaal, and Waterberg. Auriferous conglomerates are confined to the Witwatersrand series which is divided into twelve stratigraphic groups totalling 14 000 m in thickness. According to D. Pretorius the series was deposited during a time interval of 2 750-2 500 m. y. Rocks of the Witwatersrand series form an arch-shaped basin. It is a flat syncline complicated by broad folds with dip usually less than 20° being broken by a dense network of faults ranging from a few metres to 2 000 m in the magnitude of displacement. The rock series consists of a rhythmic sequence of conglomerates, sandstones and shales interbedded by andesites, quartz-feldspar porphyries and their tuffs and cut by diabase dikes.

The Witwatersrand ore bodies consist of groups of auriferous conglomerates separated by quartzite interbeds, which are known as reefs or bankets (the term "banket" is applied to commercially valuable reefs) (Fig. 125). Most of the reefs are concentrated in the upper section of the Witwatersrand series ranging from 2 000 to 4 000 m in thickness where 16 reefs are known, the most important of which are (downwards): Black, Kimberley, Bird, Leader and Main. The thickness of the reefs ranges between 30 and 400 m, and that of the auriferous conglomerates between a few centimetres and 3 m with extent reaching 70 km along the strike and 8 km down the dip. The gold-bearing beds are worked out to a depth of 3 600 m by shafts and intersected to a depth of 4 600 m by boreholes.

The gold-bearing conglomerates are oligomictic or monomictic consisting of 80% of rounded pebbles of light quartz, and more rarely of quartzite and shale pebbles, 3 to 6 cm in size, which are crushed in some places. The dark-colour cement of conglomerates is composed of quartz, chlorite, chloritoid, biotite, sericite, epidote, carbonates, carbonaceous matter, and ore minerals. 78 minerals are found in Witwatersrand ore all in all. Pyrite is most common among sulfides and the related minerals which account for 5-10% of the ore volume. Besides, marcasite, pyrrhotite, chalcopyrite, sphalerite, galena, arsenopyrite, tennantite, molybdenite, pentlandite, cobaltite, millerite, linneite, gersdorffite, skutterudite, and other minerals are present. The fragmental fraction of the rock contains chromite, zircon, spinel, garnet, xenotime, rutile, euxenite, diamond, apatite, tourmaline and monazite.

Gold, silver, platinum metals, uranium, and diamonds are recovered from the Witwatersrand ores. The gold content is 8-20 ppm, with an average of 10 ppm; the purity of gold is 900-935. Primary and secondary gold is present. Primary gold occurs in sulfides and also as fine grains 1 to 100 mμ in size in the cement. Thin films of secondary gold cut across the cement and the pebbles. Silver occurs as a native alloy with gold, as native silver, and in stromeyerite, proustite and dyscrasite. The silver content is 20 times lower than that of gold. The content of platinum-group metals varies from 3 to 30 g per 1 000 tons of ore, with the predominance of osmium (40%) and iridium (35%), and smaller amounts of ruthenium (14%), platinum (10%), rhodium (1%), and palladium (traces). These metals occur in iridosmine, iridioplatinum, sperrylite, braggite, and cooperite. Uranium is present in the amounts of 0.017-0.0628 (average 0.028% U_3O_8) in uraninite, thucholite, brannerite, and uronothorite.

Until the middle of this century many geologists (L. Graton, C. Davidson, E. Heinrich, and others) considered Witwatersrand to be a hydrothermal deposit judging from the wide development of sulfides and the presence of tetravalent uranium compounds unstable under hypergene conditions. At present this view is discarded, and Witwatersrand is classified as a Proterozoic deltaic placer which was transformed by the subsequent tectonic deformations and greenschist metamorphism with a local redistribution of the ore-forming substance (V. Domarev, V. Kotlyar, H. Bain, D. Pretorius, P. Ramdohr, H. Schneiderhöhn and others). The validity of this view is proved by the fan-like shape of the ore-bearing basin, the composition and structure of the alluvial deposits filling it, the strict confinement of ores to the fixed pebble-beds of a persistent stratigraphic position, the tendency of ore to accumulate at the base of conglomerate beds, the occurrence of ore leads in the channels of ancient streams cut into the surrounding rocks, and by the preservation of clastic placer minerals in the ores. The presence of sulfides and uraninite in the placer can be explained by a poor oxidizing effect of the specific atmosphere existing in the Proterozoic time which consisted of methane and carbon dioxide (S. Sher, 1974).

Witwatersrand is the largest gold deposit in the world. From 1887 to 1975 it produced 32 500 tons of gold, about 1 500 tons of silver, about 1 500 tons of platinum metals, and since 1953, 88 000 tons of uranium. The remaining part of the gold resources is estimated at 25 000 tons.

Metamorphic Black Shales

This group of rather widespread gold deposits includes Homestake in the USA, Juneau in Alaska, Morro Velho in Brazil, and gold deposits in Siberia, the USSR. All of them are located in so-called carbonaceous black shales of Precambrian age, the poor dispersed primary gold mineralization of which was transformed to form commercial deposits of gold ore by metamorphic processes.

HOMESTAKE. The deposit is situated in South Dakota, the USA. It is composed of a thick sequence of dark carbonaceous shales interbedded by biotite, sideroplesite-quartz, and cummingtonite-garnet-biotite schists of Proterozoic age. The rocks are crumpled into tight folds broken by small-displacement faults and cut by dikes of basic rocks converted into amphibolites.
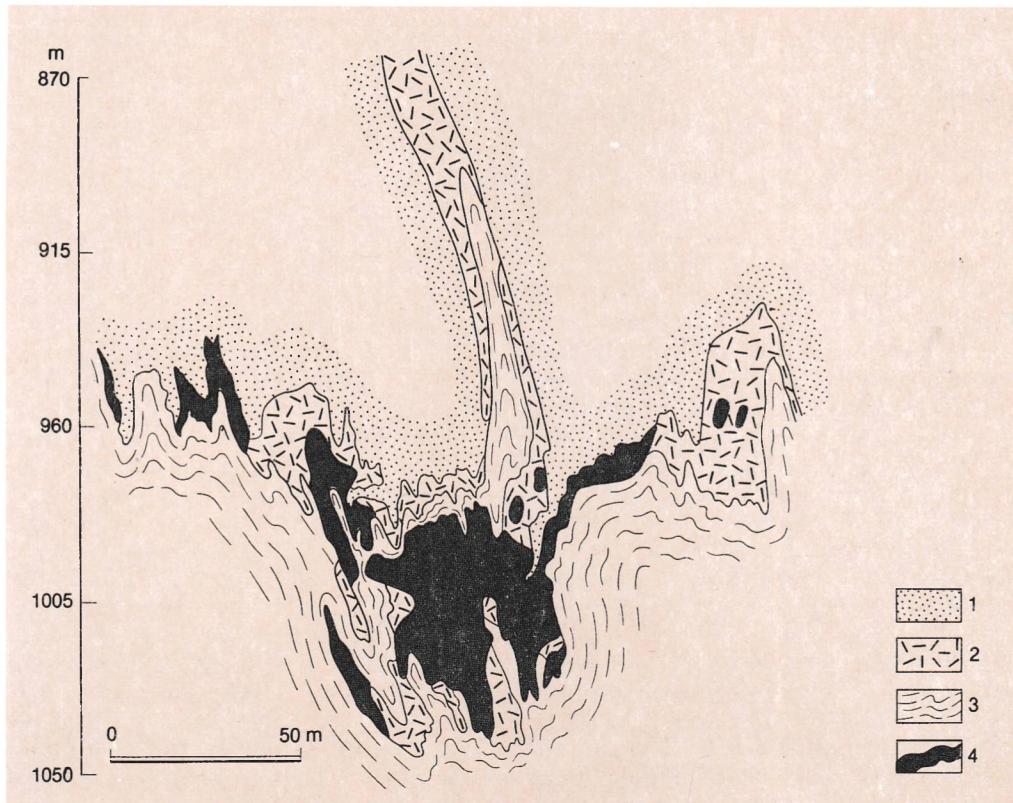
Fig. 126. Section across the Main ore body of the Homestake gold deposit. (After J. Noble):

1–Ellison formation (dark-colour phyllites);
2–Homestake formation (sideroplesite-quartz schists);
3–Poorman formation (black graphite-biotite-sericite schists);
4–ore body

The sequence of intricately deformed and dislocated Proterozoic rocks is covered by flat-lying platform deposits of Paleozoic age, and is cut together with them by Tertiary stocks, laccoliths and dikes of monzonite, rhyolite and phonolite.

Two types of ore bodies can be distinguished in the Homestake deposit (Fig. 126): (1) black shale beds with pyrite and chalcopyrite containing too little gold to be of commercial value; (2) zones of schistose biotite-chlorite rocks pierced with stringers and veins of quartz with sulfides and other minerals totalling 7-8% of the vein material (pyrrhotite, pyrite, arsenopyrite, chalcopyrite, sphalerite, galena, tetrahedrite, magnetite, ankerite, cummingtonite, sideroplesite, biotite, garnet, albite, fluorite, sericite, calcite, gypsum, and native gold). The auriferous black shale beds with low content of gold are considered to be primary. The mineralized zones of schistose rocks are described as metamorphic deposits produced, as supposed by some investigators, by regional metamorphism of a greenschist-amphibole facies, and as the other investigators believe, by the metamorphosing action of hydrothermal solutions related to Tertiary magmatism.

The Homestake deposit has been worked out to a depth of 1 900 m. It produced 900 tons of gold and 200 tons of silver, with the average gold content of 10-20 grams per ton of ore.

PLACER DEPOSITS

Placer gold deposits include alluvial, eluvial, deluvial, proluvial and littoral young and ancient placers. But only alluvial, especially valley- and terrace-type, placers are

economically significant for gold production.

Alluvial placers were formed as a result of disintegration of primary gold deposits in the process of physical and chemical weathering. In this process large grains of gold larger than 0.3-0.5 mm in size are fixed near the primary source at the base of alluvial deposits to form a gold-bearing bed. Fine-grained gold is transported down the stream to form an extensive aureole of alluvial placers traceable in river bars, which sometimes occur as far as 15 km from the primary source of gold.

TUORA TAS. This alluvial placer is located in a medium-height upland in East Siberia. The upland is a peneplain of the Paleogene and Neogene age cut by a modern drainage network. Remnants of 50-, 25-, and 5-metre terraces are preserved at the sides of the valleys. The terraces mark the successive erosion cycles of the drainage system development. The terraces of the Tuora Tas river are auriferous but the largest amounts of gold are concentrated in the valley and flood-plain placers (Fig 127).

The primary source of the placer are the quartz veins localized in a zone of a north-western trend which is cut across by the upper courses of the river and its tributaries. The initial stage of placer formation was associated with the peneplain drainage. During the subsequent erosion cycles the alluvial material was rewashed as a result of the deepening of the valleys and enriched in gold which concentrated at the bottom of the recent flood-plain deposits.

NOME. This is a unique littoral (beach) placer. It is located at the coast of the Seward Peninsula in Alaska. It was formed of delta placers which were partially rewashed in the tide land to form typical beach placers. Since the formation of placers at Nome was a long process coincident with the gradual retreat of the sea, it resulted in a series of subparallel littoral placers the outer of which is located at a height of 25 m above sea level and at a distance of 7 km from the present seashore. Twelve subparallel placers are located terrace-like down the slope towards the shore. The higher placers are partially covered by glacial and palustrine deposits, and the
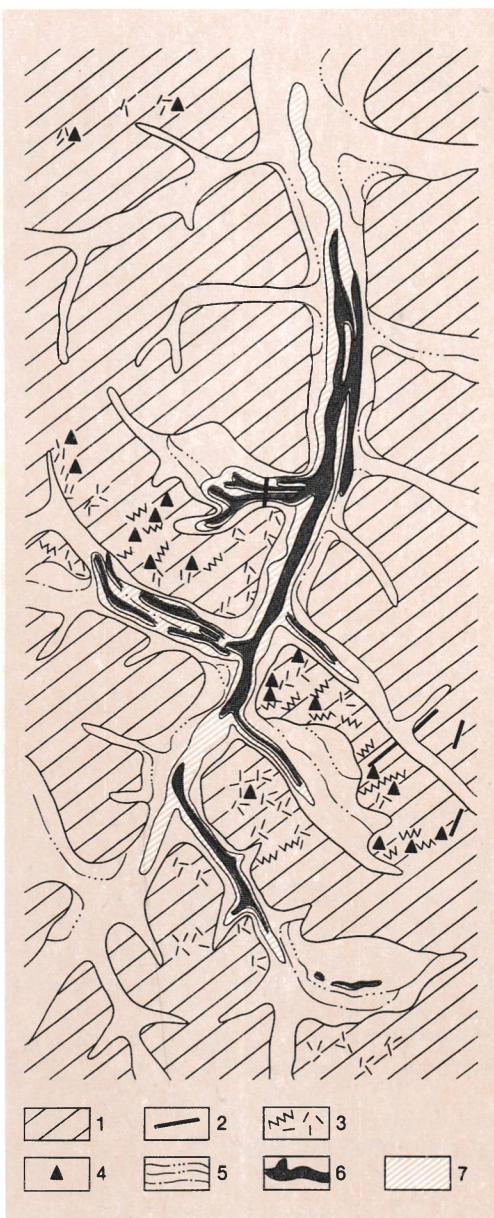
Fig. 127. The Tuora Tas placer deposit. (After Yu. Trushkov) [Conditions of Formation and Regularities of Distribution of Placers in the Mesozoic Fold Areas of Yakutia, 1971]:
1—watersheds composed of Triassic sandstones and shales;
2—dikes of igneous rocks;
3—quartz veins and their fragments;
4—gold ore occurrences;
5—edges of terraces;
6—placers of high Au content;
7—placers of low Au content
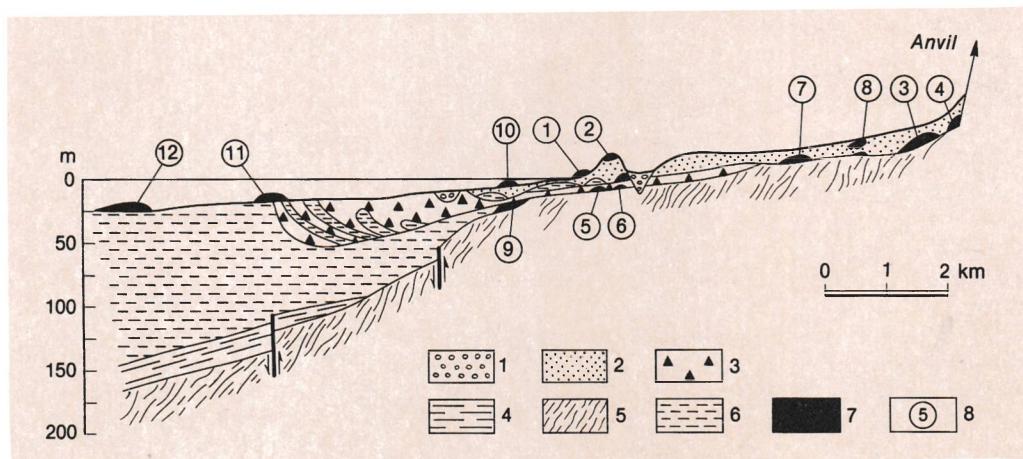
Fig. 128. Geological section across the Nome placers in Alaska. (After C. Nelson and D. Hopkins):

1–Wisconsin alluvium;
2–glacial deposits of Illinois glaciation;
3–glacial deposits of older age;
4–stratified sediments of uncertain age;
5–shales (Paleozoic);
6–marine silt and clay;
7–auriferous sea beaches;
8–sea beaches:
1–Recent;
2–Second;

3–Third;
4–Fourth;
5–Outer underwater;
6–Inner underwater;
7–Intermediate;
8–Monroeville;
9–Pliocene;
10–11-metre;
11–21-metre;
12–24-metre

lower ones by the present sea water (Fig. 128). The gold-bearing area extends 25 km along the shore and has a width of 10 km. The placers are 1-2 km in length and 100-180 m in width; the thickness of gold-bearing beds is usually 1.2 to 1.5 m occasionally reaching 5 m. The gold content is extremely variable ranging between 100 mg/m^3 and 1 000 g/m^3.

The total amount of gold recovered from the Nome placers is several tens of tons.

33 SILVER DEPOSITS

According to Pliny, Herodotus and Homer, silver is a very old metal known to ancients since 1 500 B. C. Within the territory of the USSR, it was mined as far back as the eighth-ninth centuries in Central Asia, the Caucasus, and the Carpathians. In 1978 the Nerchinskii Mines were discovered in the Transbaikal region, and in 1730–the Kolyvanskii Mines in the Altai region (M. Maksimov, 1976). The larger amount of silver (up to 70%) is used in the industry

(photographic materials, electrical and electronic products, etc.); it is used in cast silver and silver plated articles (up to 20%), in stamping and medal striking (up to 10%).

The total amount of silver recovered from the earth for the whole period of mining including 1975 was 650 thousand tons. In the last ten years the annual silver production in the capitalist and developing countries was 7-8 thous. tons. The price of silver in 1980 reached 1.5 US dollars per gram. The identified silver reserves in the capitalist and developing countries are 200 thous. tons, and the resources are estimated at 300 thous. tons.

The principal amount of the produced silver is recovered as a by-product of mining of complex silver-bearing ores. Approximately 70% of silver is obtained from the refining of poly-metallic ores, 10 to 15%–from gold-silver deposits, and only 15 to 20% of the total world production–from the deposits where silver is mined as the main product.

The silver content in base-metal ores is 10-100 ppm, in gold-silver ores is 200-1 000

ppm, and in the ores of specific silver deposits is 900-2000 ppm occasionally reaching a few tens of kilograms per ton.

GEOCHEMISTRY AND MINERALOGY

In nature silver is known to have two stable isotopes, ^{107}Ag and ^{109}Ag existing in the proportion of 51.35 and 48.65. The silver abundances (clarkes) of acidic, intermediate and basic rocks are not essentially variable being commonly estimated at $5 \cdot 10^{-6}$ to $7 \cdot 10^{-6}$. The coefficient of concentration is 1000. Being evenly distributed in the basalt and granite magmas silver does not form commercial concentrations during the magmatic stage. It concentrates in mobile post-magmatic products, most probably in the form of thiosulphate and chloride complexes forming hydrothermal deposits. Under exogenous conditions, in acidic sulphate waters inherent to oxidized zones of sulfide deposits silver passes into solution as silver sulphate or thiosulphate and is redeposited at depth as native silver or as halide. Only small amounts of silver are found in eluvial, diluvial, and short alluvial placers where it occurs as native silver.

About 60 silver and argentiferous minerals are known among sulfides, silver sulphosalts, tellurides, selenides, halides, and native elements. The principal minerals important for silver production are: native silver Ag (80-100%), argentite Ag_2S (87.1%), pyrargyrite Ag_3SbS_3 (59.8%), proustite Ag_3AsS_3 (65.4%), polybasite (Ag, Cu)$_{16}Sb_2S_{11}$ (62.1-84.9%), and stephanite Ag_5SbS_4 (68.3%). The best-known mineral – native silver – contains up to 10% gold, 6-7% copper, 1% iron, and sometimes antimony, bismuth and mercury. It occurs in hypogene and hypergene ores in the form of irregular segregations, films, wires, and dendrites, which vary in size from microscopic inclusions to nuggets reaching 20 tons in weight.

METALLOGENY

No silver deposits were formed at the early stage of a geosynclinal cycle in relation to basaltic magmatism, nor they appeared at the intermediate stage during formation of granite batholiths. The majority of hydrothermal deposits of silver-bearing polymetallic ores was formed in connection with a formation of minor hypabyssal intrusions of the late stage of a geosynclinal cycle, and most of gold-silver and silver deposits belong to a volcanic formation of the same stage.

Secondary silver deposits were formed in oxidized zones of silver-bearing sulfide ores under exogenous conditions during a platform cycle. It is likely that very rare stratiform silver deposits of the Silver Reef type (USA), which some geologists believe to be of sedimentary origin, were formed at that time.

As the silver-bearing deposits are related to a wide range of hydrothermal base-metal deposits they associate with the appropriate mineralization epochs. Volcanogenic hydrothermal silver deposits related to volcanic formations of the late stage of geosynclinal cycles first appeared in the Proterozoic and after that at the end of the Hercynian cycle, became more pronounced by the end of the Kimmerian cycle, and were abundant in volcanic complexes of the Late Alpine cycle. This governs the abundance of silver deposits in volcanic belts, especially in the American and Asiatic links of the circum-Pacific belt and in the inner arc of the Carpathians (Fig. 129).

Volcanic belts appeared on the earth by the end of geosynclinal cycles at the contacts of fold areas with platforms, or at the junctions of fold areas of different age. They consist of central- and linear-type volcanic structures, lava flows, ignimbrite and lava breccia accumulations, layers of tuff and rocks of volcanogenic-sedimentary association of continental facies, ranging from a few kilometres to 10 km in total thickness. Normally the earliest volcanic rocks were andesites and, more rarely, basalts; these were succeeded by dacites and latites which were finally followed by rhyolites to which most of the volcanogenic hydrothermal ore deposits are related. Subvolcanic bodies ranging in composition from porphyries to rhyolites, and massifs of hypabyssal

Fig. 129. Volcanic belts of America:
1–Cordillera and Andes geosyncline-fold belts;
2–volcanic belts

granitoids are associated with volcanic rocks. Volcanic belts are abundant in volcanogenic hydrothermal ore deposits including those of gold, gold-silver, and silver.

TYPES OF COMMERCIAL DEPOSITS

All silver deposits of commercial value are post-magmatic. They are divided into two categories: argentiferous deposits with by-product and co-product silver, and silver deposits with silver as a major component.

The largest amount of silver is disseminated in argentiferous deposits in which about 90% of the world's resources occur (K. Kuznetsov, R. Panfilov, 1974). The most significant of them are hydrothermal plutonogenic and especially volcanogenic

gold-silver deposits containing from a few to 500 ppm of silver including the presumably volcanogenic-sedimentary deposits of the Waterloo type, the USA. Of importance are lead-zinc-silver deposits with a silver content of 10 to 2000 ppm (Mexico). Polymetallic massive-sulfide deposits contain 100 to 350 ppm of silver. The silver content of 10 to 850 ppm is found in skarn polymetallic ores (Santa Eulalia, Mexico). Porphyry copper deposits contain 0.5 to 85 ppm of silver, and cupriferous shales – 0.5 to 250 ppm.

Most specific silver deposits are volcanogenic hydrothermal in origin; plutonogenic deposits are rare.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

In some hydrothermal plutonogenic deposits of lead-zinc, gold, and complex uranium ores, the concentration of silver is so high that it becomes a major commercial component.

MANGAZEISKII DEPOSIT. According to L. Indolev and G. Navoise (1974) this deposit belongs to a group of silver-polymetallic deposits of the Verkhoyansk ore region. The region is composed of Upper Carboniferous and Permian sandstones and shales, folded and intruded by granite and quartz porphyry stocks and dikes of the Cretaceous age to which ore formation is genetically related.

The ore field is composed of the Upper Paleozoic shales which are folded into two anticlines separated by a narrow syncline. Several interbedded silver-bearing veins have been located within the deposit (Fig. 130). The ore deposition consisted of two stages. Thin veinlets of quartz with galena, sphalerite, and tetrahedrite appeared in the first stage. During the second stage which can be divided into six sub-stages the bulk of the ores was deposited. The depositional sequence is as follows: quartz, pyrite and arsenopyrite – sub-stage I; quartz, dark aphalerite and manganosiderite – sub-stage II; quartz, galena, manganosiderite and sternbergite $(AgFeS_3)$ – sub-stage III; quartz, ankerite, freibergite $(Cu, Ag)_{12}Sb_4S$. owyheeite $(Ag_2Pb_5Sb_6S_{15})$, diaphorite

position of the mineral assemblage of the fourth (productive) substage the temperature was 300-150 °C. The Ag/Au ratio in the Mangazeiskii ores changes from 500 to 1 000.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

The majority of silver deposits are volcanogenic hydrothermal in origin. Being concentrated within volcanic belts they are usually confined to cross faults, grabens in the basement, and to zones of junction of volcanic rises with sediment-filled troughs.

The ore bodies in such deposits are often associated with the specific volcanic structures – volcanic necks and conical, circular or radial fractures. They may be localized in volcanic rocks, or subvolcanic and hypabyssal massifs, and sometimes in the basement rocks. This indicates that the source of the ore-forming material was far away. The deposits of this type were formed at shallow depth (probably from a few dozens or a few hundred metres to 2-3 kilometres) under the conditions of a sharp decrease in temperature and pressure and a rapidly increasing influence of the oxygen potential. Although the initial temperature of deposition might be as high as 600-500 °C in all the cases it decreased rapidly to be 200-100 °C and less. The environment of this kind favoured a high rate of mineral deposition within a vertically shortened interval, and contributed to the "telescopic" accumulation of complex and diverse paragenetic mineral assemblages in the ore bodies with a pronounced vertical zônality. Many high-grade veins ("precious ore formation") are substituted at a depth of a few hundred metres by compositionally simple quartz-sulfide veins with an ordinary grade of precious metals. Usually these deposits are distinguished by characteristic wall-rock alteration involving the development of successive zones of silicification and sericitization, argillization, with a gradual transition of kaolinized rocks into montmorillonized varieties. The process terminates in development of a broad aureole of propylitization and zeolitization.

Fig. 130. The geological structure of the Mangazeiskii deposit. (After L. Indolev and G. Navoise) [Silver-lead Deposits of Yakutia, 1974]:
1 – Lower Permian Echiyskii shales ($P_1e\check{c}$);
2 – Upper Carboniferous-Lower Permion Kygyltasskii eleurolite ($C_3P_1k_q$);
3 – Kygyltasskii and Echiyskii sandstone beds;
4 – quartz porphyry dikes;
5 – axes of second and higher-order anticlines (EA – Endybalskii anticline, MA – Mukhalkanskii anticline);
6 – axes of synclines (MS–Mangazeiskii syncline);
7 – faults;
8 – galena veins;
9 – carbonate-freibergite-galena veins;
10 – sulphoantimonite-sphalerite-galena veins;
11 – quartz veins

($Ag_3Pb_2Sb_3S_8$), miargyrite ($AgSbS_3$), pyrargyrite, native gold and silver – sub-stage IV; manganosiderite and light sphalerite – sub-stage V; and quartz, manganosiderite and calcite – sub-stage VI. During the de-

According to associated metals observed in volcanogenic hydrothermal silver deposits the following principal ore formations can be distinguished: (1) silver-gold, (2) silver-sulfide, (3) silver-tin, and (4) silver-arsenide.

Deposits of
Silver-gold Formation

These deposits are widespread among the similar gold and gold-silver deposits and are distinguished by the preponderance of silver over gold. In view of the fact that the price of gold is 35 times as high as that of silver, only the deposits with the Ag/Au ratio of more than 35:40 are categorized as the silver-gold ones.

Examples of silver-gold deposits are Pachuka, Guanajuato and others in Mexico; Tonopah, Comstock and others in the USA; Kohnomai, Titoci and others in Japan; and Khakanja in the USSR.

KHAKANJA. The deposit is located within the Okhotsk-Chukotka volcanic belt. According to M. Borodayevskaya and I. Rozhkov (1974), the deposit is composed of Lower Cretaceous hornblende andesites and tuffs lying on Upper Triassic and Permian flyschoid sediments. The rocks are intruded by Upper Cretaceous dacites and rhyolite-dacites of the first phase, rhyolites of the second phase, and, finally, by microgranosyenite and granite-porphyry dikes and still later basalt and dolerite dikes (Fig. 131).

Tectonic blocks composing the area are bordered by dikes and fracture zones which enclose ore-bearing quartz-adular metasomatites. The best studied Main ore zone is represented by a strip of brecciated rhyolites that are highly adularized and pierced with quartz-ore stringers.

The ore deposition consisted of two principal stages: (1) quartz-rhodonite-rhodochrosite, poor in silver, and (2) argentite-polybasite-gold (productive).

The gangue minerals are quartz, amethyst, chalcedony, adular, rhodonite, calcite, and barite; the ore minerals are pyrite, chalcopyrite, arsenopyrite, galena, sphalerite, and such specific minerals as argentite, polybasite, küstelite, pyrargyrite, pearceite, sternbergite, electrum, and gold.

The hydrothermal wall-rock alteration involves sericitization, silicification, argillization, and propylitization.
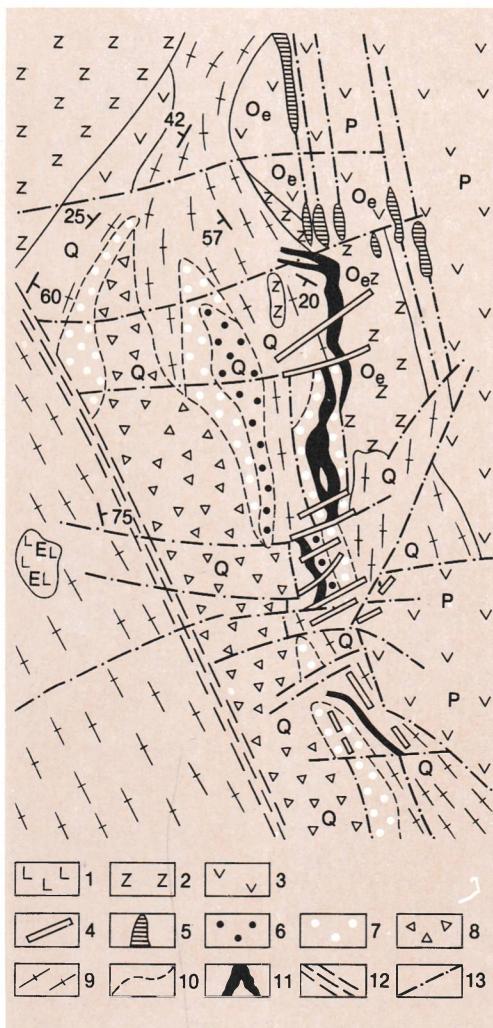
Fig. 131. Geological structure of the Khakanja deposit. [After P. Babkin and A. Sidorov (M. Borodayevskaya, I. Rozhkov, 1974)]:
1—Upper Cretaceous andesites (Cr_2);
2—dacite and rhyolite;
3—Lower Cretaceous andesites (Cr_1);
4—diabase and dolerite dikes;
5—granite porphyry and granosyenite porphyry dikes;
6—spherulitic lava;
7—spherorhyolite;
8—lava breccia;
9—fluidal and massive rhyolites;
10—boundaries of rhyolite facies;
11—ore zone;
12—sheared zone;
13—faults.
O_e—early potassium feldspathization;
E—epidotization;
P—carbonate-chlorite propylitization;
Q—hydrothermal quartzites
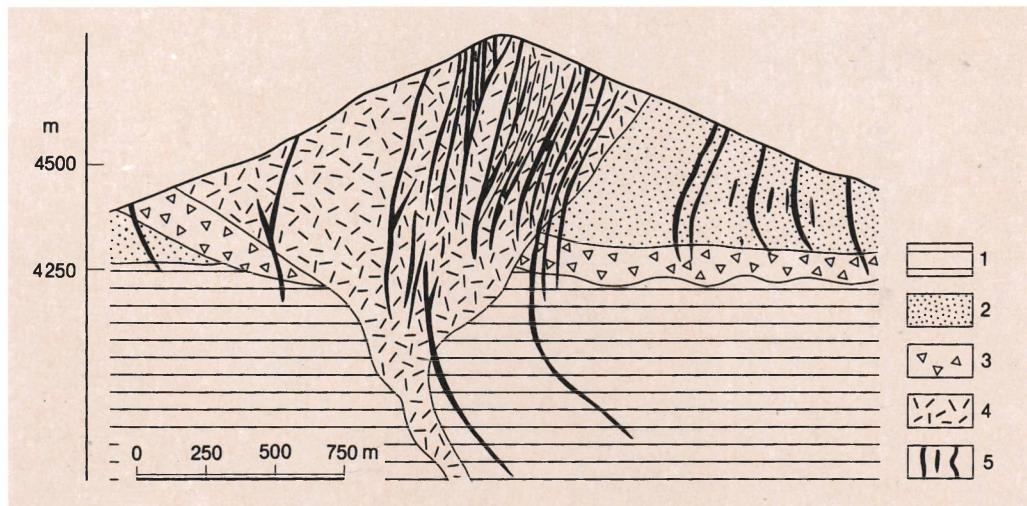
Fig. 132. Geological section across the Potosi deposit, Bolivia. (After H. Murilio):

1–Ordovician shales;
2–Tertiary volcanogenic-sedimentary rocks;
3–volcanic breccias (ignimbrites);
4–rhyolite-dacite, andesite-dacite;
5–ore-bearing veins

Deposits of Silver-sulfide Formation

Some hydrothermal volcanogenic lead and zinc deposits are so abundant in silver that they may be classified as silver ones, for example the Casapalca, Morococha and other deposits in Peru.

CASAPALCA. The published data about this and the other silver-sulfide deposits of Peru are extremely scarce. According to F. Turneaure, the major vein of Casapalca cutting the Tertiary strata extends 1 500 m on the vertical. It has a pronounced zonal structure. High-grade silver ore containing argentite and pyrargyrite which has been extensively worked out occurred in the upper part of the vein. The lower part of the vein has a zonal structure too. The core in this part of the vein is chiefly made up of chalcopyrite. Next to the core occurs a zone of rhodochrosite, sphalerite, galena, tetrahedrite, and bournonite. Antimony and arsenic sulfides are predominant in the peripheral part.

Deposits of Silver-tin Formation

The well known tin belt of Bolivia incorporates tin-bearing silver deposits; the largest deposit among them is Potosi.

POTOSI. According to F. Turneaure, the Potosi deposit is composed of flat-lying Upper Cretaceous-Tertiary volcanics resting on folded sandstones and slates of the Ordovician age. The volcanic rocks are ignimbrites, tuffs, and lavas of andesite, dacite and rhyolite compositions, totalling 1 500 m in thickness. The rocks are intruded by Middle and Late Tertiary subvolcanic diorite porphyry, porphyry and rhyolite stocks.

The ore veins are concentrated around a porphyry stock, and extend into the volcanic rocks and into the sandstones and slates of the Paleozoic basement (Fig. 132). The system of ore veins, forming one of the richest silver deposits in the world, is located here within an area of 1 km^2. The ore bodies occur as separate veins, vein clusters, and as linear zones of stringers. They vary from a few dozen metres to 350 m in length, and from 2 cm to 1 m in width. The ore bodies have been followed to a depth of 875 m; the high-grade ore extends to a depth of 350 m.

The ore deposition occurred in five stages: quartz, cassiterite, wolframite, bismuthine, arsenopyrite, and pyrrhotite were deposited during stage I; chalcopyrite and stannite were formed at stage II; sphalerite,
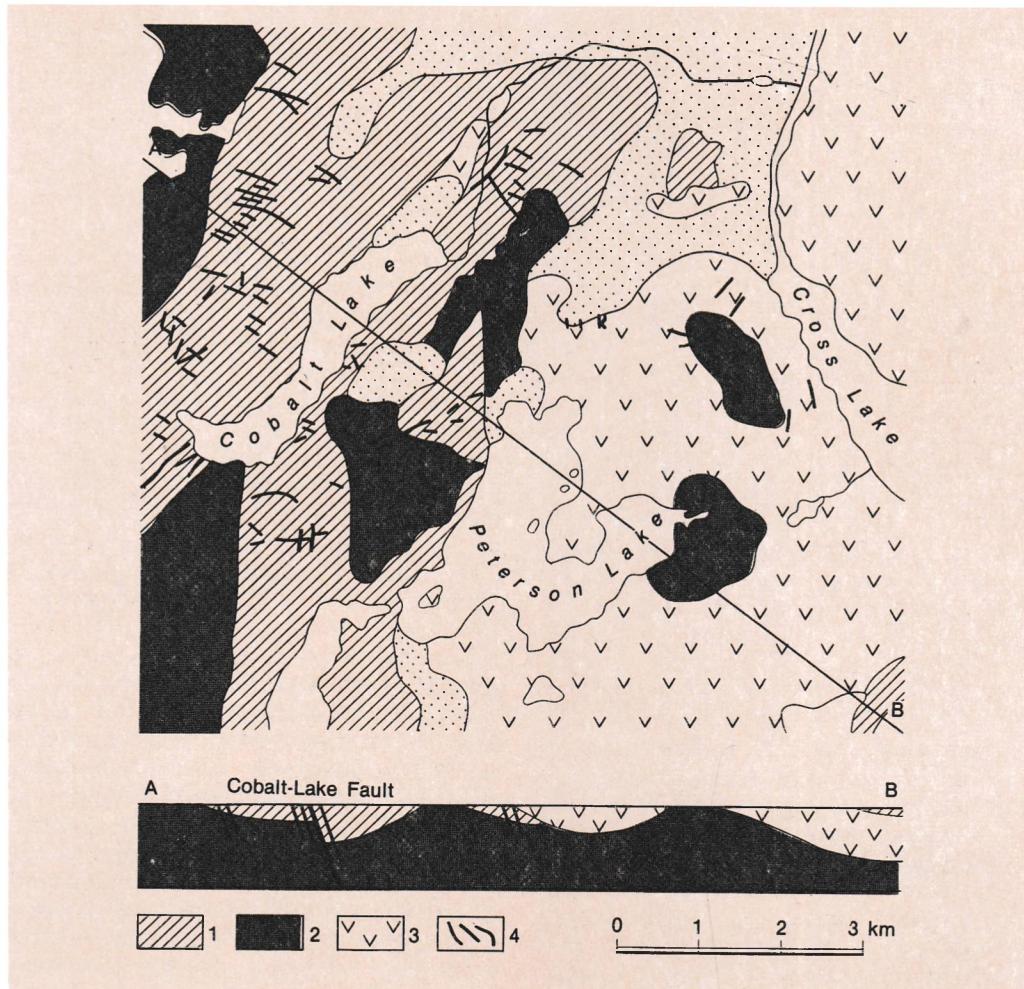
Fig. 133. Geological structure of the Cobalt deposit, Canada. After Whitehead:

1—Cobalt rocks;   3—diabase;
2—Keewatin rocks;   4—ore veins

tetrahedrite, andorite ($AgPbSb_3S_6$), and matildite ($AgBiS_2$) appeared at stage III; pyrargyrite, jamesonite, boulangerite, sphalerite, and galena were deposited at stage IV; and alunite veinlets were formed during stage V. Minerals of the early stages were deposited at 500-400 °C; later the temperature dropped to 150-100 °C.

The deep-seated wall rocks are sericitized, and those of the upper levels are silicified; besides argillization and alunitization are observed.

More than 35 thous. tons of silver have been recovered from the Potosi mine since

1544. The silver content in the ore varied from 300 to 3000 ppm; the average tin percentage is 4%.

Deposits of
Silver-arsenide Formation

The hydrothermal deposits of nickel and cobalt arsenides which may be associated with uranium and bismuth include the deposits whose ores contain silver as a most valuable component, e.g. Cobalt and Gowganda in Canada.

COBALT. The deposit is located within the Precambrian Schield. According to J. Thom-

son, the area is composed of Precambrian sedimentary and volcanic rocks intensely folded and broken by faults. The most important ore bodies are confined to one of the faults known as the Cobalt-Lake fault; they occur in the fault itself, and form a series of veins more or less parallel to it. The fault cuts across the Keewatin rocks (acidic and basic lavas interbedded by sedimentary rocks), the overlying rocks of the series Cobalt (conglomerates, greywackes, and quartzites), and a diabase sill which intruded between them (Fig. 133). The veins extend for 100-150 m and have a width of a few centimetres to 0.5 m. They usually wedge out at a depth of 30-60 m; more rarely they extend to 100 m occasionally reaching a depth of 450 m.

The ore process formation is deposited in three stages. During the first stage quartz, calcite, arsenopyrite, cobaltite, skutterudite, smaltite, safflorite, löllingite, and a small amount of bismuthite and native silver were deposited. Calcite, dolomite, niccolite, rammelsbergite, gersdorffite, chloanthite, and breithauptite appeared at the second stage. During the third stage calcite, pyrite, pyrrhotite, chalcopyrite, sphalerite, galena, bismuthine, dyscrasite, argentite, large amounts of silver sulphosalts and native silver were formed. The hydrothermal alteration of diabase resulted in the development of albite and quartz aggregates with chlorite, calcite, apatite, barite, and a small amount of sulfides.

Since 1903 when silver was discovered at Cobalt it produced more than 20 thousand tons of silver. The silver content in some veins was as high as 5%; the cobalt and nickel percentages were 8% and 14%, respectively.

34 DEPOSITS OF PLATINUM-GROUP METALS

Apart from platinum (Pt), the platinum-group metals are palladium (Pd), iridium (Ir), rhodium (Rh), osmium (Os), and ruthenium (Ru). Platinum was brought from America by the first conquistadors at the beginning of the 16th century. The earliest scientific description of platinum was made by

J. Watson in 1741. Palladium and rhodium were discovered in platinum by the British scientist W. Wollaston in 1803, and iridium and osmium by the British chemist C. Klaus in 1844.

In 1822 platinum-group metals were discovered by the mining engineer V. Lyubarskii in gold-bearing sands in the Ural Mountains in Russia, where in 1824 commercial gold-platinum placers were revealed.

Platinum-group metals are used as catalysts (50%), in the electrical engineering, automobile and medical industries (25%), in the manufacture of chemical equipment and corrosion-resistant plating (15%), and in jewelry (10%). The annual production of platinum metals in the capitalist and developing countries is 100 tons including 70 tons of platinum. In 1977 prices were (in US dollars per gram): platinum – 5, iridium – 15, rhodium – 12, osmium – 4.5, and ruthenium – 1.5. The identified reserves of platinum metals in these countries are 12.8 thous. tons, including 12.4 thous. tons in the Merensky Reef in the Bushveld complex of the South African Republic. The total resources of platinum metals are estimated at 30-40 thous. tons.

A significant amount of platinum metals (about half of the total production) is recovered in the processing of complex platinum-bearing ores of magmatic copper-nickel sulfide deposits and also mined from primary deposits of platinum metals. An insignificant amount is obtained from placers.

The primary deposits contain 3-5 to 10-15 ppm of platinum metals.

GEOCHEMISTRY AND MINERALOGY

The data available on the isotopes, crustal abundances (clarkes) and concentration factors of platinum-group elements are listed in Table 3.

Platinum metals are typical products of basaltic magma. They are separated in the process of liquation and fractional crystallization of abyssal ultrabasic and basic igneous rocks forming deposits of magmatic origin. Very few post-magmatic

Table 3. Geochemical characteristics of platinum–group elements

Geochemical parameters	Pt	Pd	Ir	Rh	Os	Ru
Number of isotopes	6	6	2	—	7	7
Crustal abundance	$5 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-7}$	$1 \cdot 10^{-7}$	$5 \cdot 10^{-6}$	$5 \cdot 10^{-7}$
Concentration factor	1 000	100	1 000	1 000	50	200

skarn and hydrothermal deposits of platinum metals are known, which are also associated with basaltic rocks. In the process of erosion, platinum metals, resistant to chemical weathering, concentrated to form placer deposits the most significant of which are localized in alluvium.

About 50 minerals of platinum metals are known. They constitute groups of native elements, disordered solid solutions, intermetallic compounds, arsenides and sulfides. Platinum, iridium, and palladium belong to the native metals. The solid solutions include polyxene Pt, Fe (77-89% Pt), ferroplatinum Fe, Pt (70-81% Pt), palladium-bearing platinum Pt, Pd (10-40% Pd), iridium-bearing platinum Pt, Ir (10-15% Ir), iridosmine-nevyanskite – Ir, Os (45-70% Ir, 30-49% Os), iridosmine – syssert-skite – Os, Ir (60% Os, 30% Ir), and rhodium nevyanskite Ir, Os, Rh, (70% Ir, 17% Os, 11% Rh). Representatives of the intermetal group are aurides, e. g. cupro-auride (Cu, Pd)$_3$Au$_2$, stannides, e. g. niggliite (Pt, Pd)$_3$Sn, bismuthides, e. g. frudite PdBi$_2$, plumbides, and tellurides. A representative of arsenides is sperrylite PtAs$_2$ (56.5% Pt), and those of sulfides are cooperite PtS (79-86% Pt), braggite (Pt, Pd, Ni)S (32-58%Pt, 17-38% Pd), vysotskite (Pd, Ni)S (59.5% Pd), hollingworthite (Rh, Pt) (As, S)$_2$ (20% Pt, 25% Rh), and laurite RuS$_2$ (61-65% Ru).

METALLOGENY

In a general course of geological development, deposits of platinum metals were formed at the early stage of a geosynclinal cycle, and in the periods of reactivation during a platform cycle. At the early stage of a geosynclinal cycle magmatic deposits of chromospinellides containing platinum and palladium were formed in association with dunites, as the extreme

differentiates of a gabbro formation, and magmatic accumulations of osmium and iridium were produced in association with ultrabasic differentiates of a peridotite formation.

In the process of platforms reactivation two groups of deposits were formed: (1) magmatic copper-nickel sulfide deposits containing palladium, platinum, and lesser amounts of the other metals of the group were formed in deeply differentiated parts of a trap formation; and (2) early- and late-magmatic deposits of platinum-bearing chromites were formed in relation to stratiform norite complexes, e. g. the Merensky Reef in the Bushveld Complex, the South African Republic.

Deposits of platinum metals were formed in the Archean (Australia), Proterozoic, Paleozoic, Mesozoic, and Cenozoic (minor deposits of the Mediterranean and Pacific belt). Yet, two principal epochs of their formation, Proterozoic and Hercynian, are recognized as the most important. The magmatic liquation-type deposits of Canada, the Cola Peninsula (USSR), and South Africa (Bushveld Complex) were formed in the Proterozoic epoch. The magmatic deposits of platinum-bearing chromospi-nellides of the Urals and magmatic liquation-type sulfide deposits of Siberia (Noril'sk) appeared in the Hercynian epoch.

TYPES OF COMMERCIAL DEPOSITS

Four types of platinum-metal commercial deposits are known: (1) liquation-type, (2) early magmatic, (3) late magmatic, and (4) placers.

LIQUATION DEPOSITS

Platinum metals are recovered from liquation copper-nickel sulfide deposits as
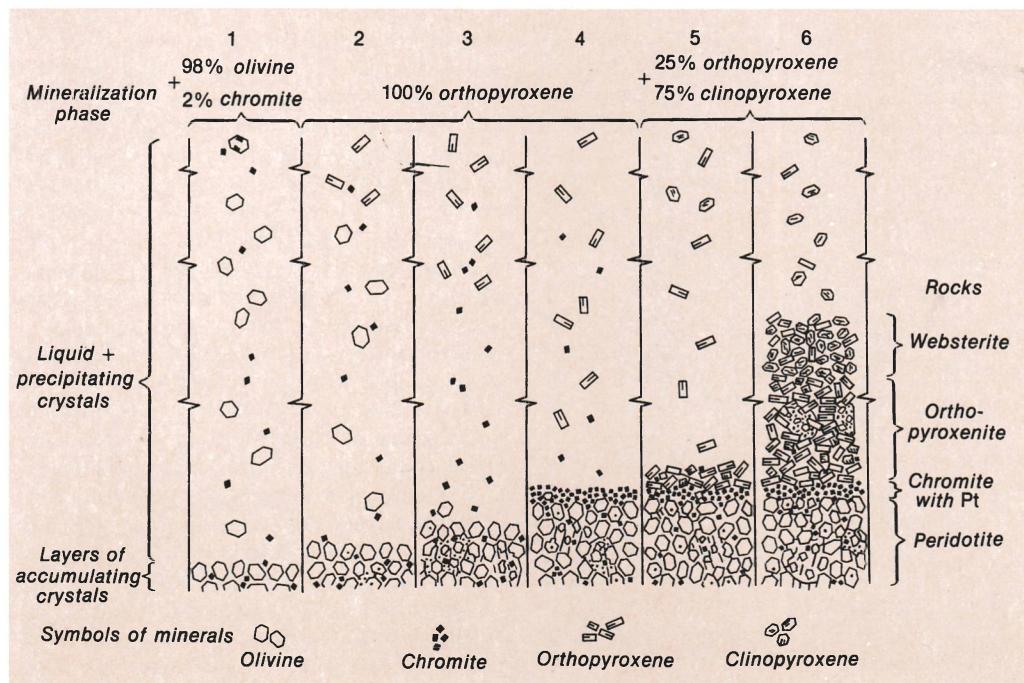
Fig. 134. A model of formation of early magmatic deposits of platinum-bearing chromite of the Merensky Reef. (After C. Cousins)

valuable by-products in nickel and copper production.

The content of platinum metals in the ores varies from place to place. In some deposits it ranges from hundredth to tenth fractions of a gram per ton, in some it is from one to ten grams per ton, and in the others it can be even more than ten grams per ton. For instance, their concentrations reach 5-20 ppm at the deep levels of the Frood Mine in the Sudbury deposit, Canada.

The most abundant of platinum metals is palladium (65-72%); next come platinum (15-25%) and rhodium (up to 10%); the shares of the remaining metals are a few per cent.

A significant amount of platinum metals occurs as a fine admixture in ore-forming sulfides which is mineralogically unidentifiable. The remainder is represented by minute platinum-group minerals 20 to 100 mμ in size occasionally reaching a few millimetres. Being intergrown with sulfides (pyrrhotite, pentlandite, chalcopyrite) they precipitate at the final stage of crystallization of the sulfide substance.

The principal minerals of palladium are its disordered solid solutions and intermetallic compounds with platinum, tin, lead, nickel, cobalt, copper, and bismuth. Besides, palladium arsenides and tellurides are known. Platinum is represented by its native form, solid solutions, arsenides, and sulfides. Minerals of rhodium and iridium are very rare, and those of ruthenium and osmium have not been discovered.

The description of liquation copper-nickel sulfide deposits is given in the Chapter "Deposits of Nickel".

EARLY MAGMATIC DEPOSITS

Segregations of platinum metals usually associated with chromospinellides are known in dunite of ultrabasic series of the early stage of a geosynclinal cycle, in a dunite fraction of massifs of the central type composed of ultrabasic-alkaline rocks with carbonatites, and in stratified norite
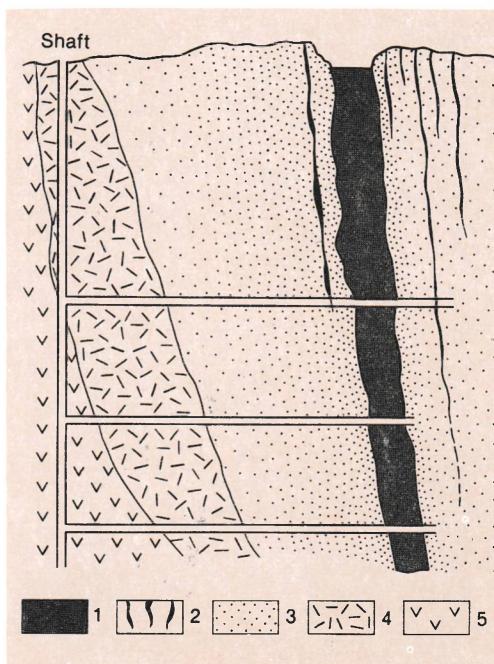
Fig. 135. The Mooihoek platinum-bearing pipe. (After A. Bateman):

1 – hortonolite dunite with chromite and platinum-group metals accumulations;
2–hortonolite dunite dikes;
3–olivine dunite;
4–pyroxenite;
5–norite

massifs. Commonly they do not reach a commercial grade. The exception are the large deposits of platinum metals in the Merensky Reef within the Bushveld Complex, the South African Republic.

MERENSKY REEF. The Merensky Reef and the related platinum-metal deposits occur in the Bushveld Complex which incorporates large chromite deposits described in the chapter on chromium.

This is a huge Proterozoic complex of stratiform rocks including the Critical zone of interstratified norites, pyroxenites and anorthosites about 1 000 m thick, which incorporates the Merensky Reef composed of diallage norite. The lower portion of the Reef includes a flat-lying ore layer concordant with the host rocks and persistently extending for dozens of kilometres. It has been studied in more detail in the Rustenburg, Potgietersrust, and Lydenburg localities. In Rustenburg, this

layer, 20 to 45 cm thick, rests with a sharp contact on anorthosite norite and is overlain by pyroxenite. The ore consists of harzburgite with orthopyroxene, bytownite, biotite, chromite, magnetite, and ilmenite, which are accompanied by patches of disseminated pyrrhotite, pentlandite, chalcopyrite, cubanite, millerite, valleriite, and nickeliferous pyrite. The platinum-group minerals are ferro-platinum, braggite, cooperite, sperrylite, laurite, and bismuth tellurides of platinum and palladium. Gold is present.

With the content of platinum metals in the ore reaching 15-20 ppm, they are distributed as follows (in % of the total): platinum – 60, palladium – 27, ruthenium – 5, rhodium – 2.7, iridium – 0.7, osmium – 0.6, and gold – 4.

The segregation type of ore mineral accumulation, and the textural and structural features of the ore allow C. Cousins and other investigators to classify them as early magmatic cumulate formations (Fig. 134).

The isolated masses of massive and disseminated sulfide ores in bronzitite, consisting of pyrrhotite, pentlandite and chalcopyrite and containing platinum metals, known in the Blackfontain locality, were probably formed as a result of partial liquation of a metalliferous magma melt.

LATE MAGMATIC DEPOSITS

Late magmatic deposits of platinum metals are associated with accumulations of chromospinellides in a dunite fraction of basic intrusives. They are represented by ore bodies cutting across the lithologic boundaries whose ores are distinguished by a sideronitic texture which indicates that the ore minerals were deposited after the rock-forming silicates had been crystallized.

LYDENBURG. The Lydenburg district contains steeply dipping pipes of platinum-bearing dunite, which cut across a sequence of flat-lying igneous rocks of the stratified Bushveld Complex. The pipes, 10 to 100 m in diameter, extend to a depth of 300 m. The central ore zone consists of hortonolite dunite surrounded by a fringe zone of olivine dunite and by an outer fringe of pyroxenite (Fig. 135). The ore includes iron-rich olivine, and subordinate amounts of phlogopite, hornblende, diallage, ilmenite,

magnetite, chromite, and platinum metals. The platinum metal content increases upwards and toward the centre of the ore-bearing pipes ranging from 2 to 30 ppm and reaching 60 ppm and more where the olivine rock has a pegmatoid appearance owing to large hornblende and biotite crystals.

Skarn and hydrothermal occurrences of platinum mineralization which occur at the periphery of the Bushveld Complex, are genetically associated with it. Skarns are known in the Potgietersrust region where the Bushveld igneous rocks contact dolomites. A grossular-diopside zone with sperrylite, cooperite, and stibiopalladinite, which contains up to 10 ppm of platinum metals extends along the contact. A hydrothermal quartz vein with specularite and pyrite containing platinum and iridium is known to occur in the Waterburg dolomites.

So, the formation of platinum-group metal deposits in the Bushveld Complex was a long process. At the early stage concordant stratiform early magmatic deposits were formed, and at the late stage cross-cutting late magmatic bodies were probably formed of the residual melts. Late magmatic deposits were formed under active influence of fluids which continued to act in the post-magmatic processes. These fluids were responsible for the appearance of skarn and hydrothermal platinum mineralization in the post-magmatic period. H. Schneiderhöhn considered it to be a secondary mineralization produced by the redeposition of the Bushveld magmatic platinum metals by late hydrothermal solutions.

NIZHNI-TAGIL. This typical deposit of platinum-group metals is a part of the platinum belt of the Urals which is marked by a chain of Middle Paleozoic early-geosynclinal ultrabasic rocks controlled by the deep-seated fault. The Nizhni Tagil massif is an example of completely differentiated complexes. The central part of the massif is composed of platinum-bearing dunite which in places is serpentinized. It is surrounded by a zone of pyroxenites followed outwards by a gabbro zone (Fig. 136).

Platinum-group metals occur in two forms: (1) a low-grade dissemination
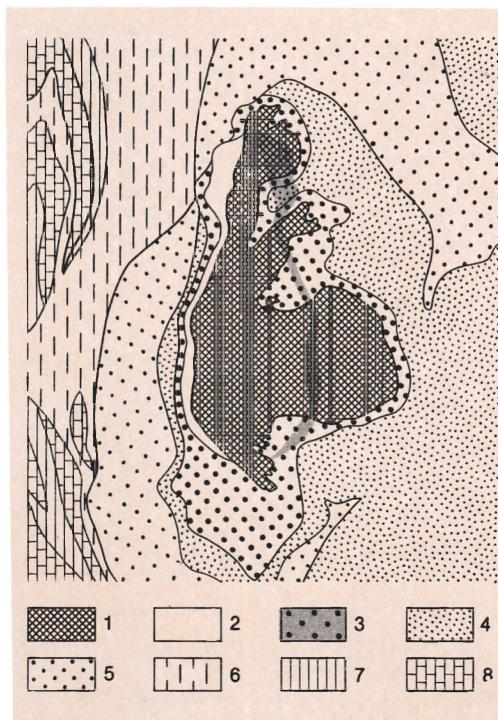
Fig. 136. Geological structure of the Nizhni-Tagil platinum-bearing massif. (After N. Vysotskii):
1–dunite with chrome-spinellides and platinum-group metals accumulations;
2–apodunite serprentinites;
3–pyroxenites;
4–gabbro;
5–apogabbro amphibolites;
6–mica schists;
7–crystalline schists;
8–limestones

throughout the dunite field; and (2) in pockets and pipes of chromite enriched in platinum minerals the most abundant of which are polyxene and iridioplatinum, and less common are iridosmine, platinum-bearing iridium, laurite and stibiopalladinite. Pentlandite and cubanite are also observed.

N. Vysotskii considered the ores to be primary segregation-type concentrations of early magmatic origin. A. Karpinskii supposed the Nizhni Tagil pipes to be of explosive origin. A. Zavaritskii pointed out that platinum minerals were crystallized after orthosilicates as a result of the decomposition of complex metallic compounds. And finally, A. Betekhtin proved

that the platinum minerals, xenomorphic with respect to chromo-spinellides, were deposited from the residual magma melt forming late magmatic deposits. Furthermore, this melt rich in mineralizers was responsible for the appearance of chrome-garnets, chrome-chlorites, and chrome-tourmaline, and for the development of serpentinization zones.

PLACER DEPOSITS

Eluvial, diluvial and alluvial placers of platinum minerals are known in the USSR, the USA, Columbia, Zimbabwe, Zaire, Ethiopia, and in other countries. The most economically important are Late Quaternary placers which extend in river valleys for a few kilometres and in some places for dozens of kilometres. They were formed as a result of the disintegration of platinum-bearing massifs of a gabbro-pyroxenite-dunite formation containing low-grade but extensive primary mineralization.

The placer deposits of platinum minerals contain polyxene, platinum, ferroplatinum, cuproplatinum, iridioplatinum, nevyanskite, ruthenium nevyanskite, and iridium and platinum gold. The content of platinum minerals in alluvial placers varies from a few milligrams to several hundred grams per cubic metre.

Platinum minerals are also known in Precambrian ore-bearing conglomerates, e. g. in Witwatersrand, the South African Republic, which are considered to be metamorphosed fossil delta placers. The main minerals there are iridium, platinum iridium, sperrylite, braggite, and cooperite.

REFERENCES TO "PRECIOUS METALS" SECTION

Betekhtin, A. G. Platinum and Platinum-group Minerals. Moscow, USSR Ac. Sci. Publishers, 1935.

Bilibin, Yu. A. Fundamentals of Placer Geology. GONTI, 1938.

Borodayevskaya, M. B., Rozhkov, I. S. Gold Deposits. In: *The USSR Mineral Deposits*. V. 3, 2nd edition, revised and enlarged. Ed. Academician V. I. Smirnov. Moscow, Nedra, 1978.

Borodayevskii, N. I., Borodayevskaya, M. B. The Berezovskii Ore Field. Moscow, Metallurgizdat, 1947.

Boyle, R. W. The Geochemistry of Silver and Its Deposits.– *Bull. of Geol. Surv. of Canada,* No. 6, 1968.

Boyle, R. W. The Geochemistry of Gold and Its Deposits.– *Geol. Survey of Canada,* 1979.

Emmons, W. H. Gold Deposits of the World. New-York and London, Mc Graw-Hill Book Co., 1937.

Indolev, L. N., Nevoise, G. G. Silver-lead Deposits of Yakutia. Moscow, Nauka, 1974.

Kuznetsov, K. F., Panfilov, R. V. Silver Deposits. In: *The USSR Mineral Deposits,* V. 3, 2d edition, revised and enlarged. Ed. Academician V. I. Smirnov. Moscow, Nedra, 1978.

Magmatic Ore Deposits. Translation from English. Ed. V. I. Smirnov. Moscow, Nedra Publishers, 1973.

Nesterenko, G. V. Origin of Placer Deposits. Novosibirsk, Nauka,, 1977.

Petrovskaya, N. V. Native Gold. Moscow, Nauka, 1973.

Razin, L. V. Deposits of Platinum Metals. In: *The USSR Mineral Deposits.* V. 3, 2d edition, revised and enlarged. Ed. Academician V. I. Smirnov. Moscow, Nedra, 1978.

Sher, S. D. Metallogeny of Gold. Moscow, Nedra.– North America, Australia, Oceania, 1972. – Eurasia, Africa, South America, 1974.

Vysotskii, N. K. Platinum and Regions of Its Production. Parts 1–5. Petrograd-Leningrad, KEPS Ac. Sci. Publishers, 1923–1933.

RADIOACTIVE ELEMENTS

> Economically valuable natural radioactive elements are uranium, thorium, and radium. Below follows the description of uranium and thorium deposits.

35 URANIUM DEPOSITS

Uranium was discovered in 1789 by the German chemist M. Klaproth in pitchblende from a mine in Saxony. Radioactivity was discovered in 1896 by the French physicist A. Backeray. It was discovered and formulated in 1898 by P. Curie and Mme Marie Curie when they discovered radium and polonium in association with uranium. The extraction of radium from uranium ore began in 1914. In 1939 D. Danning proved natural nuclear fission of radioactive elements. In 1942 this discovery opened the way for the use of uranium as a powerful source of nuclear energy.

The U_3O_8 production (with the uranium conversion factor of 0.85) in the capitalist and developing countries was 27 thous. tons in 1976; the production is expected to be as high as 80-90 thous. tons by 1985.

The total demand for uranium in these countries was 24.5 thous. tons in 1976. According to the data of the International Atomic Energy Agency, uranium requirements are expected to be 40-50 thous. tons in 1980, 85-100 thous. tons – in 1985, and 200-800 thous. tons – in the year of 2 000 (*Formation of Uranium Deposits*, 1976).

The resources of uranium in these countries are estimated for different prices. The prospected reserves of relatively high-grade ores are estimated at one million tons for the price of 22 US dollars per one kg U_3O_8. The uranium reserves in lower-grade minable ores amount to 1.3 million tons for the price of 33 US dollars per one kg, and in the ores of still lower grades – two million tons for the price of 60 US dollars per one kg. The total reserves are 2-2.5 times more. The estimated reserves are concentrated in the deposits of the USA, Australia, Canada, the South African Republic, Namibia, Niger, France, Spain, and Portugal. Besides, about 100 thousand tons of U_3O_8 are available at the stocks of the uranium-production nations.

The uranium deposits containing more than 10 thous. tons of U_3O_8 are classified as large ones, one to ten thous. tons – as medium ones, and less than one thous. tons – as small ones.

GEOCHEMISTRY AND MINERALOGY

Uranium consists of three natural isotopes: ^{238}U (99.2739%) having a half-life of $4.51 \cdot 10^{-9}$ years, ^{235}U (0.7024%) with a half-life of $7.3 \cdot 10^8$ years, and ^{234}U (0.0057%) with a half-life of $2.48 \cdot 10^5$ years.

The isotopes ^{238}U and ^{235}U are generators of two radioactive series. The natural decay of ^{238}U produces a series (uranium family) of protactinium, thorium, radium, radon, astatine, polonium, bismuth, mercury, and thallium, which terminates in accumulation of the stable isotope ^{206}Pb. The ^{235}U series (actinium family) consists of protactinium, thorium, actinium, radium, francium, radon, astatine, polonium, bis-

muth, and helium; the series is completed by separation of the isotope ^{207}Pb.

The crustal abundance (clarke) of uranium is $2.5 \cdot 10^{-4}\%$. The average abundances increase markedly from ultrabasic to basic and acidic rocks: $3 \cdot 10^{-7}\%$ for ultrabasic, $5 \cdot 10^{-5}\%$ for basic, and $3.5 \cdot 10^{-4}\%$ for acidic rocks. The concentration factor for uranium is 400 for the average U content of 0.1% in the mined ore.

In chemistry uranium has valencies of 3, 4, 5, and 6. In nature uranium may be tetravalent and hexavalent. The ions of tetra and hexavalent uranium have an eight-electron outer shell structure, and hence are lithophile, have a great affinity for oxygen, and are found in nature only as oxides or in salts of oxygen acids. It is essential that tetravalent compounds are poorly soluble and precipitate, while hexavalent forms are sufficiently soluble facilitating uranium migration. Fig. 137 shows the relationship between tetra- and hexavalent uranium oxides in water solutions as a function of pH and Eh (under equal conditions). Uranium does not concentrate in endogenous processes at a magmatic stage in association with the products of basalt magma.

At the early stage of granite magma crystallization, in reducing and alkaline environments, tetravalent uranium compounds enter rock-forming minerals chiefly as isomorphous admixtures and are dispersed to form a relatively high uranium abundance in granites. The highest uranium concentrations (up to 50% of the total quantity) are observed in accessory minerals of relatively high radioactivity, such as sphene, orthite, monazite, zircon, apatite, ilmenite and others. The principal rock-forming minerals, particularly dark ones, contain 5 to 15% of the total amount of U; and the remaining amount of uranium is present in microinclusions and in intergranular seams. In multiphase granite intrusions uranium concentration increases from the early stages to the late ones [A. Smyslov, 1974], reaching the highest values in the final highly acidic and alkaline differentiates (up to $10\text{-}50 \cdot 10^{-4}\%$).

At the late stage of granite magma crystallization characterized by an increasing oxidation potential, uranium passes into the
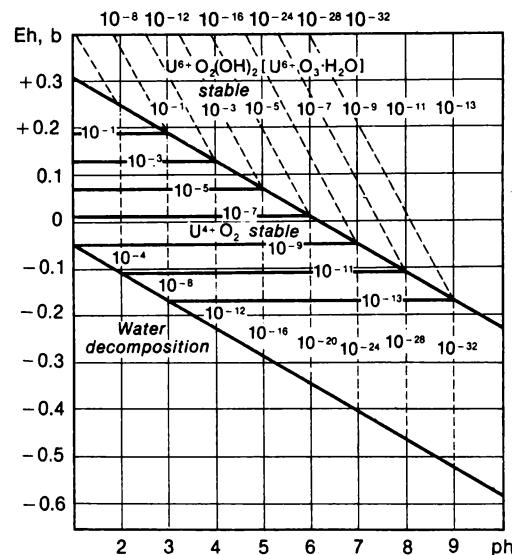
Fig. 137. Fields of stability of tetravalent and hexavalent uranium as a function of acidity-alkalinity (pH) and oxidation-reduction (Eh) conditions. (After R. Garrels)

hexavalent state, is dissolved in a volatile phase, and is removed by hydrothermal solutions. According to G. Naumov [1978], uranium is transported by hydrothermal solutions chiefly in the form of uranyl carbonate complexes of the $Na_4[UO_2(CO_3)_3]$ type and to a lesser degree in the form of uranyl sulphate, uranyl phosphate, uranyl silicate, and other complexes. As a result of degassing and mixing of the solutions, change in their acidity along with variations in temperatures and pressures, and of the interaction of the solutions with surrounding rocks, complex compounds decompose and tetravalent uranium compounds are released and precipitate to form hydrothermal ore bodies which compose significant endogenous uranium deposits.

In the oxidizing environment of exogenous conditions, tetravalent uranium compounds become unstable and change to hexavalent ones. According to V. Danchev, A. Perelman and other investigators, uranium is hydrolized to form a complex bivalent cation-uranyl, $[UO_2]^2$, whose high mobility makes it extremely important in the migration and concentration of uranium

in exogenous conditions. As a consequence, water-soluble complexes of uranyl tricarbonate $[UO_2(CO_3)]^4$, uranyl diaquadicarbonate $[UO_2(CO_3)_2H_2O]$, uranyl hydroxide $UO_2(OH)_2$ and more rare uranyl humate, uranyl phosphate, and silicon uranyl are formed in neutral and alkaline environments in surface and near-surface ground waters. A water-soluble complex of uranyl sulphate, $(UO_2)(SO_4)^2_2$ or $(UO_2)(SO_4)^4_3$, may be formed in an acidic sulphuric environment.

Under these conditions uranium is leached out of the near-surface parts of endogenous ore bodies consisting of tetravalent uranium compounds and is partially removed beyond the ore bodies and redeposited at depth in zones of secondary oxidized and reduced ores. The resulting succession of sulfide-bearing uranium ores is formed as follows (downward): a surface layer with opal which adsorbed uranium, a zone of uranium silicates, a zone of uranium sulphate-carbonates, and a zone of secondary regenerated uranium oxide minerals. In nonsulfide deposits at the surface, uranium is fixed in silicates, and somewhat below in hydroxide compounds.

Uranium is leached out of primary deposits and rocks in a form of water-soluble complex compounds to be released to surface water solutions. In the course of run-off and infiltration of such waters, uranium could precipitate again in the processes of sorption and reduction. It may be adsorbed by organic substances (peat, humus, decaying animal and plant remnants), or by hydrocarbons of petroleum and coal origin, and may be precipitated with phosphates, glauconite, clay, iron hydroxides and other surface products, thus creating the basis for sedimentary ore formation. Where infiltrating uranium-bearing waters pass from oxidizing to reducing conditions, secondary ore bodies of an infiltration type are formed at reduction barriers, which exhibit an oxidation-reduction zoning.

The amount of uranium decreases with the increasing degree of metamorphism. As estimated by A. Smyslov [1974], the rocks of a greenschist facies contain $2.8 \cdot 10^{-4}\%$ U,

of an amphibolic facies $-1.6 \cdot 10^{-4}\%$ U, and of a granulite facies -0.4 to $1 \cdot 10^{-4}\%$ U. This fact is explained by gradual removal of uranium along with increasing metamorphism.

About 100 uranium and uranium-bearing minerals are known in nature. Of greatest practical value is uraninite (nasturan, pitchblende) UO_2 (92%) and its amorphous variety (up to 60%)*.

Various types of minable ores include:

	%
brannerite (U, Ca, Th, Y) $[(Ti, Fe)_2O_6]$	(28-44)
davidite (Fe, U) TiO_3	(20)
uranothorite (Th, Fe, U)$SiO_4 \cdot nH_2O$	(up to 17)
uranophane $CaH_2[UO_2(SiO_4)]_2 \times \times 5H_2O$	(67)
coffinite $U(SiO_4)_{1-x} \cdot (OH)_{4x}$	(68)
autunite $Ca[UO_2 \cdot PO_4]_2 \cdot 10- -12H_2O$	(60)
torbernite $Cu[UO_2PO_4]_2 \cdot 8- -12H_2O$	(61)
zeunerite $Cu[UO_2AsO_4]_2 \cdot 10H_2O$	(56)
carnotite $K_2[(UO_2)_2V_2O_8] \cdot 3H_2O$	(64)

METALLOGENY

No endogenous uranium deposits are formed at the early stage of a geosynclinal cycle in relation to basaltoid intrusive or extrusive magmatism. By contrast, sedimentary rocks of the early stage are essential for uranium mineralization. Two uraniferous associations are formed during this stage: (1) carbonaceous-silicate association of black shales enriched in organic matter and carrying disseminated uranium mineralization; (2) phosphatic sandstones also with disseminated uranium mineralization. Having been formed at the early stage of a geosynclinal cycle they served as the reserves which could be subsequently transformed into commercial uranium deposits of magmatogenous and metamorphogenous origin.

The intermediate stage of a geosynclinal cycle with its granite batholiths was also poorly productive as to the formation of uranium deposits.

The late stage is the most productive. The

---

* Hereinafter the term "uraninite" includes nasturan and pitchblende.

bulk of plutonogenic hydrothermal deposits is associated with hypabyssal intrusions of this stage, and the majority of volcanogenic hydrothermal deposits of uranium ores are related to a volcanic andesite-rhyolite formation. Early molasse formations of this stage contain uranium deposits of an infiltration type.

During a platform cycle both plutonogenic and volcanogenic hydrothermal uranium deposits were formed in areas of tectono-magmatic reactivation. At the same time infiltration deposits were formed in late molasses in foremountain and intermountain basins, and sedimentary deposits appeared in terrigenous, carbonate, carbonaceous and bituminous sediments.

The oldest uranium deposits were formed in the Early Proterozoic cycle of geological development, mainly in the time interval of 2.8 to 2 billion years marked by the formation of uranium-bearing conglomerates. Uranium-bearing pegmatites and albitites and the earliest hydrothermal uranium deposits were formed during the Late Proterozoic cycle. During the Caledonian cycle uranium-bearing black shales were developed, which are especially characteristic of the Silurian time. Endogenous mineralization in that epoch was weak. Rather abundant plutonogenic and volcanogenic uranium deposits appeared during the Hercynian cycle. During the Alpine cycle deposits of these two classes continued to form mainly in regions of tectonic and igneous reactivation, and exogenous deposits were formed in the sedimentary formation of foremountain and intermountain basins.

Two characteristic features can be recognized in the geologic history of formation of uranium ore deposits: first, the tendency of endogenous deposits to be confined to rigid blocks of regional geological structures – intrageoanticlines, median massifs, consolidated areas of completed folding, and platforms – and the related control of their localization by deep faults; second, the coincidence of the areas of sedimentary and subsequent hydrothermal ore formation, which suggests that part of the ore-forming material of endogeous deposits could be derived from sedimentary com-

plexes. This suggestion does not rule out the contribution of independent deep magmatogenous portions of ore-forming uranium [V. Kazanskii et al, 1978].

TYPES OF COMMERCIAL DEPOSITS

All commercial types of uranium deposits can be divided into (1) albitite; (2) plutonogenic hydrothermal; (3) volcanogenic hydrothermal; (4) sedimentary; (5) infiltration; and (6) metamorphogenic.

ALBITITE DEPOSITS

Albitite uranium deposits are known to occur in metamorphic complexes of Precambrian crystalline rocks (Fig. 138).

According to V. Krupennikov [Uranium and Rare Metal Deposits, 1976], one of the deposits of this kind is confined to a deep fault separating an area of Proterozoic granites from that of Archean gneisses. The intrusion of granites having an age of 2 billion years was succeeded by the intrusion of alkaline porphyroblastic granites (1.8-1.7 billion years) which are accompanied by pegmatites.

A thick zone of blastocataclasites and blastomylonites was formed along the fault separating granites and gneisses, which was subjected to sodium metasomatism resulting in formation of albitites carrying uranium mineralization. Alkaline amphiboles or epidote with chlorite are predominant in the outer portion of the metasomatic zone, microcline and albite – in the intermediate zone, and albite – in the inner, most U-rich zone.

The ore bodies have a shape of flattened lenses and pipes composed chiefly of albite. They also contain zircon, apatite, quartz, aegirine, riebeckite-rhodusite, epidote, chlorite, hydrobiotite, and carbonates. The uranium minerals are represented by uranotitanates, uraninite, davidite, coffinite, hydronasturan, uranophane, and betauranotil. Ilmenite, magnetite, hematite, pyrite, pyrrhotite, chalcopyrite, bornite, and galena may be present. Two stages of ore deposition can be recognized. The bulk of albite with uranium minerals was
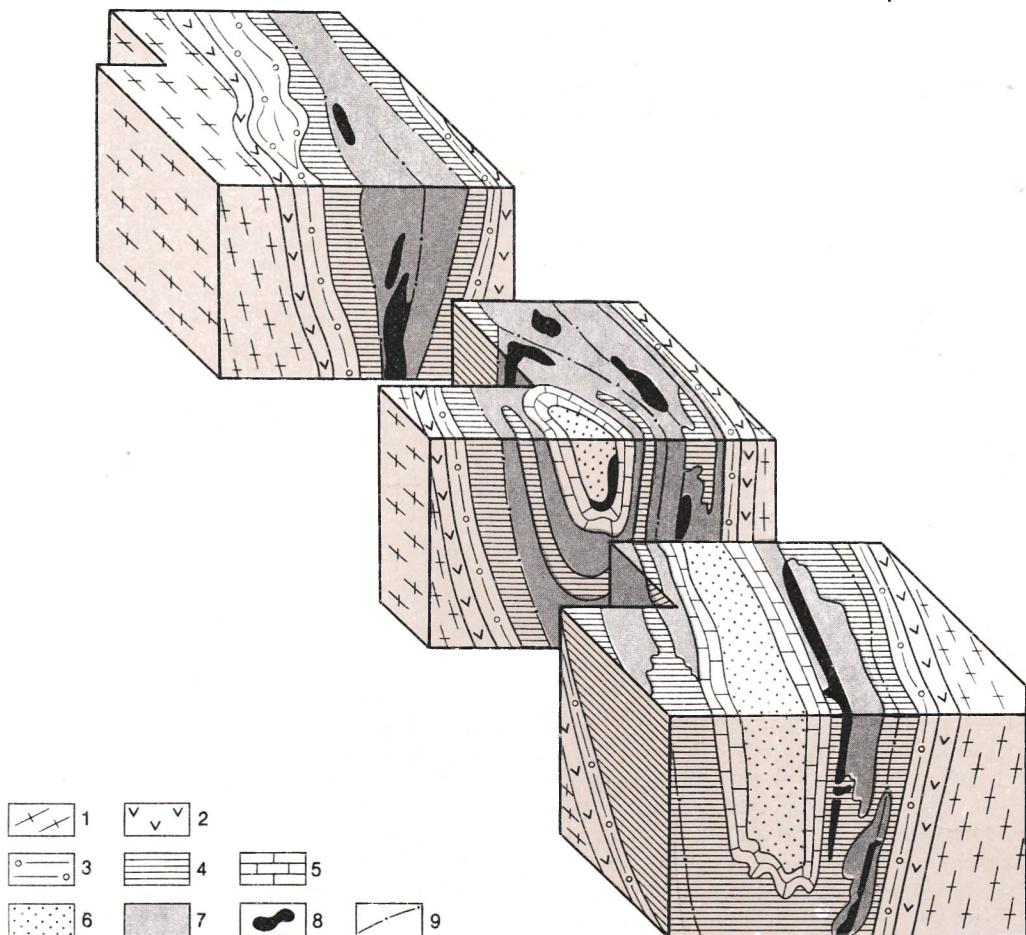
Fig. 138. Geological structure of an albitite uranium deposit. (After V. Kushev) [Uranium and Rare-metal Deposits, 1976]:

1–granite gneiss;
2–amphibolite;
3–garnet-biotite and garnet-amphibole schist;
4–iron quartzite;
5–marmorized carbonate rock;

6–quartzite and schist;
7–albitite;
8–uranium ore;
9–tectonic fault

deposited during the early stage, and quartz with sulfides during the late stage.

Formation of uranium-bearing albitites began at 400-350 °C and continued at a temperature gradually decreasing to 200-150 °C by the end of the process when the deposition of late quartz and carbonates began. Some geologists (Ya. Belevtsev and others) consider uranium-bearing albitites as the products of Proterozoic metamorphism, and the others (V. Kazanskii, N. Laverov) believe them to be hydrothermal products associated with latest granite intrusions.

PLUTONOGENIC HYDROTHERMAL DEPOSITS

Plutonogenic hydrothermal deposits were of essential economic value when the uranium industry just started to develop. Later they were superseded by the other types of uranium ores. Plutonogenic uranium deposits of the Proterozoic, Paleozoic, Mesozoic, and Cenozoic age are known. Most common among them are uranium-bearing veins occurring as fissure fillings; metasomatic ore bodies are rare. Usually such deposits are found in areas of development of late geosynclinal and

post-geosynclinal hypabyssal granitoids to which they are directly or indirectly genetically related. A direct relation means that granitoids served as a direct source of post-magmatic hydrothermal ore-forming material, and an indirect relation implies that granitoids generated a heat energy and heated ground waters, which extracted ore-forming elements from the surrounding rocks and redeposited them in ore bodies.

Two principal formations can be distinguished in the deposits of this type, uraninite-sulfide and uraninite-arsenide.

Deposits of Uraninite-sulfide Formation

Apart from uraninite, the ores of this formation include sulfides. Most common is pyrite, and various combinations of chalcopyrite, bornite, molybdenite, bismuthine, sphalerite, galena, and grey ore may be present. The most common and ubiquitous gangue mineral is quartz; carbonates are frequently found; fluorite and barite are occasionally present.

MARYSVALE. This deposit is situated in Utah, the USA. The area is composed of a sequence of limestones, quartzites, sandstones and shales of the Permian, Triassic and Jurassic age covered by the lower extrusive series of andesite-porphyry composition of the Tertiary age. The gently folded complex of sedimentary and volcanic rocks totalling about 3 thousand metres in thickness is intruded by Tertiary monzonites and granites, which are in turn partially covered by a sheet of rhyolite lavas constituting the upper extrusive series.

Ore bodies occur within an area of 0.5 to 1 km^2 (Fig. 139). They are concentrated in monzonites and in some places extend into rhyolites. They occur as steeply dipping veins reaching 500 m in length, ranging between 1.5-2 and 7 m in width and extending to a depth of 800 m. The veins are composed of uraninite associated with pyrite, and magnetite, fluorite, adular and quartz; umohoite $UO_2 \cdot MoO_4 \cdot 4H_2O$ was also found. Hypergene minerals – hydrous silicates, carbonates, phosphates, and sulphates – occur in the upper parts of the veins to a depth of 60 m.
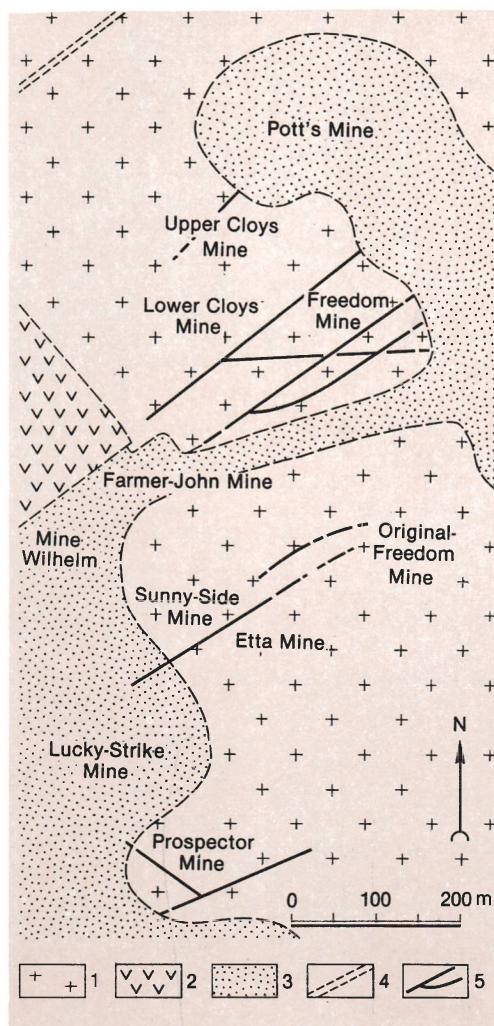
Fig. 139. Geological structure of the Marysvale deposit. (After P. Kerr):
1–monzonite;
2–granite;
3–rhyolite;
4–rhyolite dike;
5–ore vein

Uranium mineralization is accompanied by hydrothermal alteration of the host rocks extending in 0.5- to 3-metre zones on both sides of the veins. Argillization prevails in the inner zone, and chloritization in the outer one.

It is likely that ore deposition started right after granite intrusion and continued till the time when the granites were partially covered by rhyolites.

During a 20-year period of mining Marysvale has produced 275 thousand tons of ore with an average content of 0.2% U_3O_8.

LIMOUSIN. This deposit is situated in the middle of the Central Plateau, France. It occurs together with the other similar uranium deposits related to Hercynian granites, which were formed in three phases, from porphyry granites of the early phase to two-mica granites of the final one.

According to V. Kotlyar, the geological setting of the deposit is controlled by a system of strike-slip faults of a north-western strike, which cut across the eastern margin of a granite massif. The main ore body is a lens-like deposit of intensely mineralized granite breccias squeezed between two faults gently dipping to the north-east spaced 300 m apart. The body is about 400 m in length and up to 25 m in width; it has been traced to a depth of 400 m. The ore consists of hydrothermally altered granite fragments cemented by quartz with colloform uraninite and sulfide segregation.

The history of ore deposition consists of five stages. The first stage consisted in formation and silicification of granite breccias, the second – in formation of quartz and carbonate veinlets, the third – in deposition of quartz with uraninite, pyrite and chalcopyrite, the fourth – in additional deposition of quartz and hematite with fine inclusions of uraninite, marcasite and pyrite, and the fifth – in deposition of quartz with pyrite, chalcopyrite and bismuthinite.

Alteration of the host granites is manifested in silicification and hematitization. Torbernite, autunite and other uranium phosphates occur in the oxidized zone.

The U_3O_8 reserves are estimated at 6 thoudand tons with an average content of about 0.35% U_3O_8 in the mined ore.

Deposits of
Uraninite-arsenide Formation

The ores of this formation are distinguished by a complex composition, a perceptible content of nickel and cobalt arsenides and silver minerals. The most complete mineral assemblage is found in the so-called penta-element formation which include uranium, nickel, cobalt, bismuth and silver minerals. Commonly, this series of elements lacks some of its constituents.

PORT RADIUM. The deposit is situated at the eastern shore of Great Bear Lake in Canada. According to D. Campbell, the area is composed of Precambrian metamorphic rocks. The roch succession consists of metamorphosed quartzites, conglomerates and andesite lavas and tuffs intruded by granites.

The rocks in the ore field itself are chert shales and quartzites covered by stratified tuffs and cut by flat hypabyssal bodies of porphyries and diabase dikes. Volcanic and sedimentary rocks surrounding the intrusives are transformed into various hornfels. Massive biotite granites are located to the west of the deposit.

The rocks are folded and cut by large strike-slip faults of a north-eastern strike. Some of the higher-order fractures associated with the faults are filled with ore, thus forming the deposit. A field of ore veins extends 4 km in a north-eastern direction with a width of about one km. The ore veins and vein zones vary from a few hundred metres to 2 km in length and from a few centimetres to 10 m in width. They have been traced to a depth of 700 m. Some of them are simple veins filling separate shear fractures, and the others are complex vein zones controlled by belts of fractured rocks. Ore shoots occur in the swelled portions of the veins produced in the curved ore-bearing fractures pulled apart by tension, especially where they pass from one rock type into another (Fig. 140).

Uraninite occurs in colloform segregations forming massive lenses, stringers, fringes and minute dispersed inclusions. Among arsenides are safflorite-rammelsbergite, smaltite-chloanthite, skutterudite, cobaltite, löllingite, gersdorffite, and glaucodot. Sulfides and their analogues are pyrite, chalcopyrite, bornite, arsenopyrite, cobaltite, molybdenite, sphalerite, galena, and polydymite, as well as hematite, tetrahedrite, freibergite, and native bismuth. The silver minerals are argentite, hessite, stromeyerite,
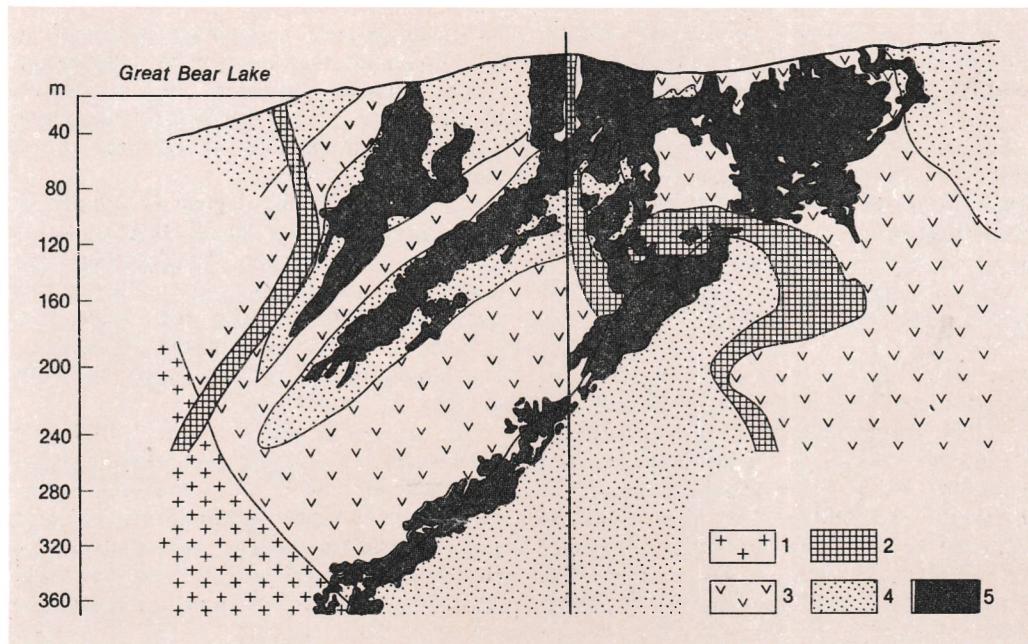
Fig. 140. Ore shoots on the longitudinal projection of vein 3 in the Port Radium deposit. (After D. Campbell):

1 – granite;   *3* – porphyry;   *5* – ore
2 – diabase;   *4* – sedimentary rock;

altaite, and native silver. The most abundant gangue minerals are quartz, dolomite, barite, witherite, and manganocalcite.

The ore deposition occurred in five stages. Quartz and hematite were deposited at stage I, uraninite was added at stage II, the bulk of cobalt-nickel arsenides was deposited during stage III, sulfides were crystallized during stage IV, and carbonates and silver minerals most abundant in the upper parts of the veins were deposited during stage V. The wall-rock alteration is manifested in argillization, chloritization, hematitization and carbonatization.

VOLCANOGENIC HYDROTHERMAL DEPOSITS

Volcanogenic hydrothermal uranium deposits are associated with volcanic complexes of late geosynclinal and post-geosynclinal stages of the geological history, mainly of the Hercynian and Alpine cycles. The complexes consist of pyroclastic layers, lava sheets, sills, subvolcanic bodies,

and hypabyssal massifs of an andesite-rhyolite-trachyte formation. Since these deposits were formed under near-surface conditions a substantial contribution into the ore deposition was made by vadose waters activized by the heat energy of volcanoes. They are distinguished by the presence of volcanotectonic structures of volcanic stratification, necks, collapse calderas, and specific fissure systems developed in the intravolcanic and peripheral volcanic zones. Breccia and colloform structures of ores are common.

V. Kotlyar [Radioactive and Rare-metal Deposits, 1973] divided the class of volcanogenic hydrothermal uranium deposits into the following ore associations: (1) uranium-titanium (davidite, brannerite): (2) uraninite-galena; (3) uraninite-molybdenite: (4) uraninite-fluorite; (5) uraninite-chalcopyrite; (6) uraninite-arsenic; (7) uraninite-apatite; and (8) uraninite-allophane. Below follow examples of the first four formations.

Deposits of
Uranium-titanium Formation

This group includes uranium deposits in which the major minerals are brannerite or davidite (Fig. 141).

V. Krupennikov et al. [*Uranium and Rare-metal Deposits*, 1976] describe a uranium deposit occurring in crystalline schists and gneisses in a Precambrian platform which underwent tectonic and igneous reactivation in the Mesozoic time. The complex of volcanic rocks thus produced consists of trachyte sheets, trachyte tuff beds, subvolcanic syenite bodies, and lamprophyre dikes. The age of the rocks is 160 ± 110 m. y. It corresponds to the age of brannerite mineralization (145 ± 20 m. y.), which allows one to correlate this deposit with the Mesozoic episode of volcanic activity and to classify it with some uncertainty as a volcanogenic hydrothermal deposit.

The ore bodies are confined to the arcuate parts of major faults running in Precambrian crystalline rocks. The faults were formed in the Precambrian as blastomylonite zones and were rejuvenated during Mesozoic reactivation, when ore-bearing exfoliation and breccia zones were formed. The ore bodies occur in the form of veins, lenses, linear stockworks, pipes, and pockets. The ore deposition consisted in five stages. During the first stage (250-225 °C) the rocks adjacent to the ore-bearing faults and the breccias occurring within the faults underwent pre-ore metasomatism with the development of orthoclase, quartz, carbonates and pyrite. During the second stage (300-225 °C) albite-quartz-barite veinlets were formed bearing small amounts of pyrite, chalcopyrite, sphalerite and galena. Brannerite and small amounts of pitchblende, rutile, sphene, biotite, adular, microcline, quartz, and pyrite were deposited during the third stage (about 200 °C). During the fourth stage (220-170 °C) quartz with magnetite and sulfides (pyrrhotite, pyrite, chalcopyrite, sphalerite, galena, and grey ore) were added. Quartz, barite, fluorite and carbonates were deposited during the fifth stage (175-95 °C). The ore bodies were formed in a depth
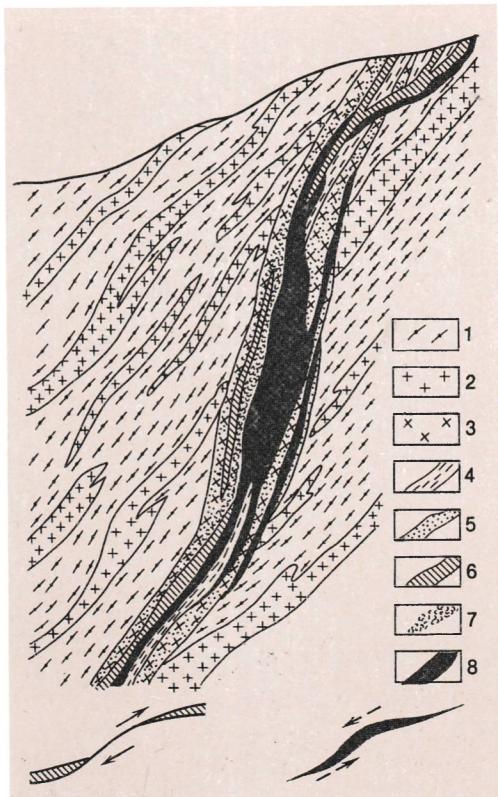
Fig. 141. Geological section across the deposit of a uranium-titanium association. (After V. Krupennikov et al.) [*Uranium and Rare-metal Deposits*, 1976]:

1–crystalline schists and gneisses;
2–granites;
3–quartz-feldspar rocks;
4–blastomylonite in diorite dikes;
5–pyrite-carbonate-feldspar metasomatites;
6–barite-quartz veins;
7–barite-quartz stringers;
8–ore bodies; direction of fault displacements during formation of barite-quartz veins and ores

interval of 0.8 to 2 km below the ground surface [V. Kazanskii, N. Laverov, 1978]. The ore-enclosing crystalline schists and gneisses are replaced by potassium feldspar near the ore bodies and are chloritized, sericitized and carbonatized farther outwards.

Deposits of
Uraninite-galena Formation

In the deposits of this type, uraninite is associated with sulfides of which galena is most abundnat (Fig. 142). N. Laverov et al [*Uranium and Rare-metal Deposits*, 1976] describe a deposit localized in a sequence of
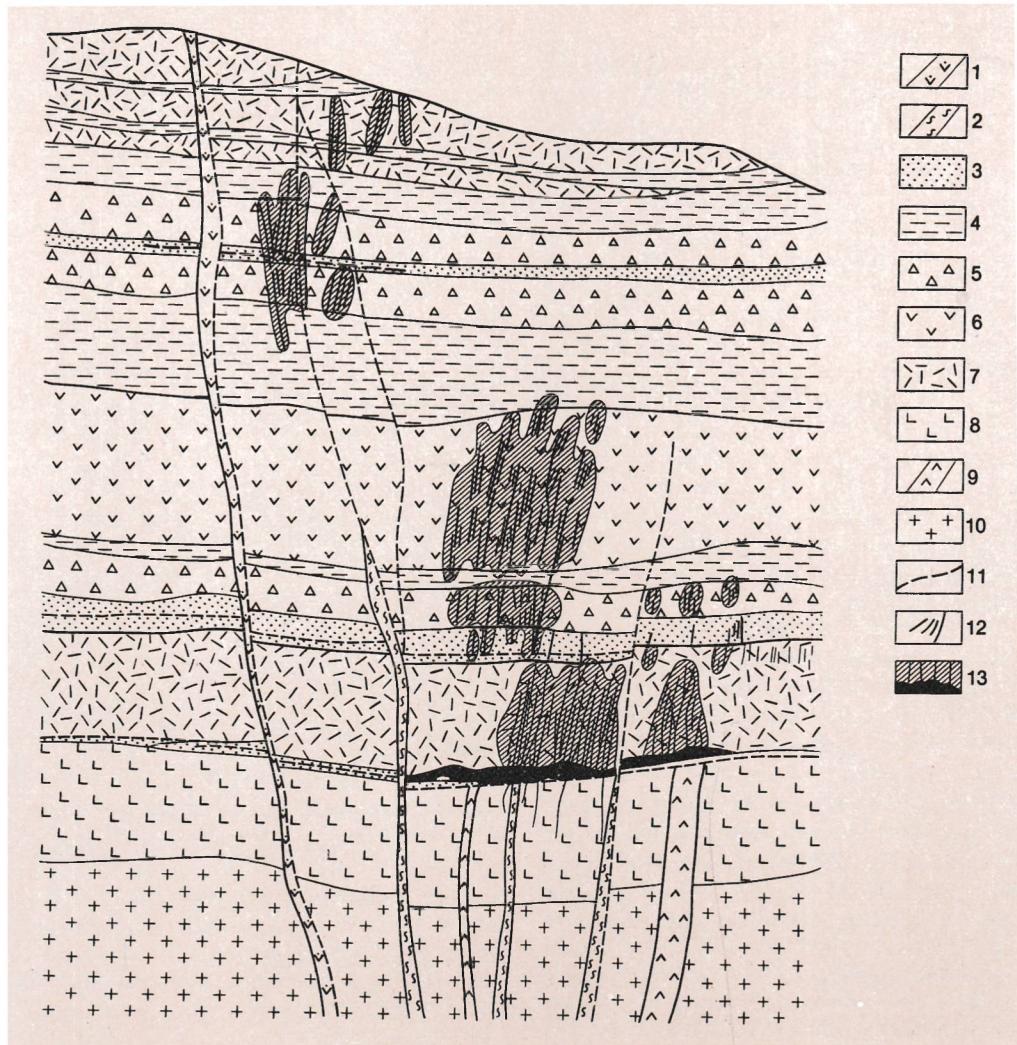
Fig. 142. Geological section across a deposit of uraninite-galena association. (After N. Laverov et al.) [Uranium and Rare-metal Deposits, 1976]:

1 – quartz parphyry dikes;
2 – felsite dikes;
3 – tuffites, tuffaceous sandstones, agglomerates;
4 – rhyolite ignimbrites and quartz porphyry lavas;
5 – rhyolite tuff breccias;
6 – crystalloclastic quartz porphyry tuffs;
7 – quartz porphyry tuffs with ignimbrite interbeds;

8 – andesite agglomerate lavas;
9 – granodiorite-porphyry and andesite dikes;
10 – granites;
11 – joints;
12 – uraninite veins and veinlets;
13 – ore bodies: blanket veins; stockworks

volcanogenic-sedimentary rocks in a caldera depression formed over the rigid granite basement. The rock sequence totalling about 1 000 m in thickness starts with lavas and pyroclastic rocks of andesite composition and is crowned by pyroclastic and extrusive rhyolites. Large and extensive linear faults and local ring fracture zones cut across the whole sequence of volcanic rocks.

Mineralization is localized in layers of highly porous tuffs and tuff breccias where they are intersected by fracture zones. The ore bodies have a form of veins, linear stockworks and sheets. The ores deposited
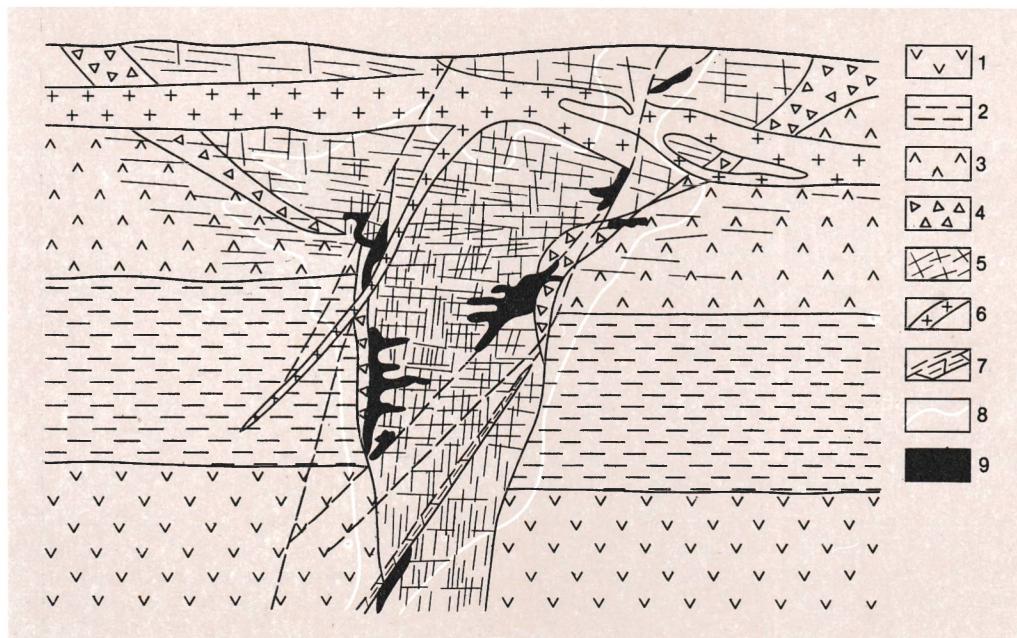
Fig. 143. Geological section across the deposit of a uraninite-molybdenite association. (After N. Laverov et al.) [Uranium and Rare-metal Deposits, 1976]:

1—massive felsite-porphyry sheet;
2—fluidal felsite-porphyry sheet;
3—ignimbrite sheet;
4—neck eruptive felsite breccias;
5—neck felsites;
6—granite-porphyry dikes;
7—faults;
8—contours of altered rocks;
9—ore bodies

in three stages. During the first stage quartz-sericite patches with carbonate, barite, fluorite and first-generation galena were formed. Albite, hematite, uraninite, second-generation galena, pyrite, and small amounts of coffinite, molybdenite, marcasite, sphalerite, chalcopyrite and grey ore were added at the second stage. During the third stage calcite, fluorite, third-generation galena, and small amounts of pyrite and sphalerite were deposited. The amount of sulfides increases with depth.

Pre-ore hydrothermal alteration of volcanic rocks involved albitization and silicification. Co-ore alteration has a zonal pattern with chlorite and carbonates developed in the inner zone, argillite – in the intermediate, and hematite – in the outer zone. Mineralization extends to a depth of 500-700 m. The ores were deposited at a depth of not more than 200-300 m below the ground surface at a temperature of 180-170 °C.

Deposits of
Uraninite-molybdenite Formation

Deposits of this formation occur in submarine and surface volcanic complexes. They are usually confined to hypabyssal stocks, necks, volcanic domes, and stratified sequences of andesite, dacite, trachyandesite, felsite and rhyolite lava sheets and pyroclastic beds.

An example of near-surface deposits (Fig. 143) is described by N. Laverov et al [*Uranium and Rare-metal Deposits*, 1976]. The deposit is localized in a neck of an ancient volcano which broke through a sequence of Paleozoic post-geosynclinal volcanic rocks which are represented by andesites and dacites at the base, and felsites at the top. The volcanic vent is filled with explosive felsite breccias of variable permeability. The volcanic edifice and the adjacent layered felsites are cut by dikes and sills of diabase, diorite and granite porphyry. The whole complex of igneous

rocks is broken by steeply dipping branching faults.

The ore bodies are localized in the volcanic vent, at its contacts with the surrounding rocks, and where the relatively porous felsite breccias are cut by faults and covered by more compact impermeable rocks. The ore occurs in stockworks, stocks and pockets. Small sheet-like ore bodies are found where mineralization penetrated the surrounding stratiform volcanic rocks. Mineralization was preceded by hydrothermal quartz-albite alteration of the host rocks.

The subsequent ore deposition occurred in four stages. During the first stage (400-300 °C) a network of quartz-tourmaline-biotite veinlets in places including rutile and muscovite was formed. Beresites consisting of quartz, sericite, chlorite, leucoxene, pyrite, arsenopyrite, and calcite appeared at the second stage (about 300 °C). During the third stage (220-210 °C) uraninite was deposited in association with coffinite, molybdenite and insignificant amounts of other sulfides (pyrite, marcasite, arsenopyrite, chalcopyrite, and grey ore). During the fourth stage (200-190 °C) calcite was added which was accompanied by quartz, sericite, chlorite, pyrite, hematite, and posterior uraninite portions.

Deposits of Uraninite-fluorite Formation

A deposit of this type described by N. Laverov et al [*Uranium and Rare-metal Deposits*, 1976] is located in an area whose geologic section consists of Paleozoic metamorphic rocks and granitoids covered by flat-lying volcanic rocks of the Late Mesozoic age (Fig. 144). The ore-bearing volcanic succession filling a large caldera starts with andesite basalt which is succeeded by dacite interstratified with sandstones and aleurolites and terminates in massive felsites, ignimbrites, breccias and tuffs. The column of volcanic rocks is cut by granosyenite porphyry and rhyolite stocks and andesite dikes and is broken by gently and steeply dipping faults. The steeply dipping faults extend into the Paleozoic basement breaking the ore deposit into blocks.

The ore occurs in stockworks, sheet-like bodies and vein zones. Stockworks are concentrated where volcanic and sedimentary layers favourable for ore deposition are cut by faults. Sheet-like ore bodies occur at the plane detachments between volcanic and sedimentary layers. The ore veins are widespread throughout the sequence of volcanogenic-sedimentary rocks and in some places extend into the granites of the Paleozoic basement, which is indicative of a deep-seated source of ore mineralization.

The ore was deposited in three stages. During the first stage (350-300 °C) quartz-carbonate (ankerite, siderite, dolomite) veinlets containing pyrite, arsenopyrite and molybdenite were formed. During the second stage (200-150 °C) quartz and uraninite were deposited, and coffinite, bertrandite, hematite, molybdenite, jordisite, pyrite, sphalerite, galena, and löllingite were crystallized. During the third stage (150-80 °C) quartz-fluorite mass was formed, accompanied by adular, chlorite, hydromica, calcite, ankerite, siderite, pyrite, and posterior portions of uraninite.

The ore deposition occurred in a depth interval of 300 to 1 500 m.

SEDIMENTARY DEPOSITS

Origination of sedimentary uranium deposits was related to the reduction and sorption of mobile uranium compounds in a depositional environment. The principal reductants and sorbents are carbonates, phosphorites, zeolites, hard bitumens, carbonaceous matter, and plant detritus. The mineralization products of a primary sorption were transformed during diagenesis and acted as a mineral substance of a sedimentary-diagenetic process. The sedimentary-diagenetic uranium deposits of this kind are known to occur in sedimentary strata of the Paleozoic, Mesozoic and Cenozoic age. Older deposits usually belong to the metamorphogenic type. Since mineralized sedimentary rocks are spread over extensive areas the uranium reserves in such deposits are voluminous but often contain low-grade ores owing to a limited sorption capacity of the rocks involved.
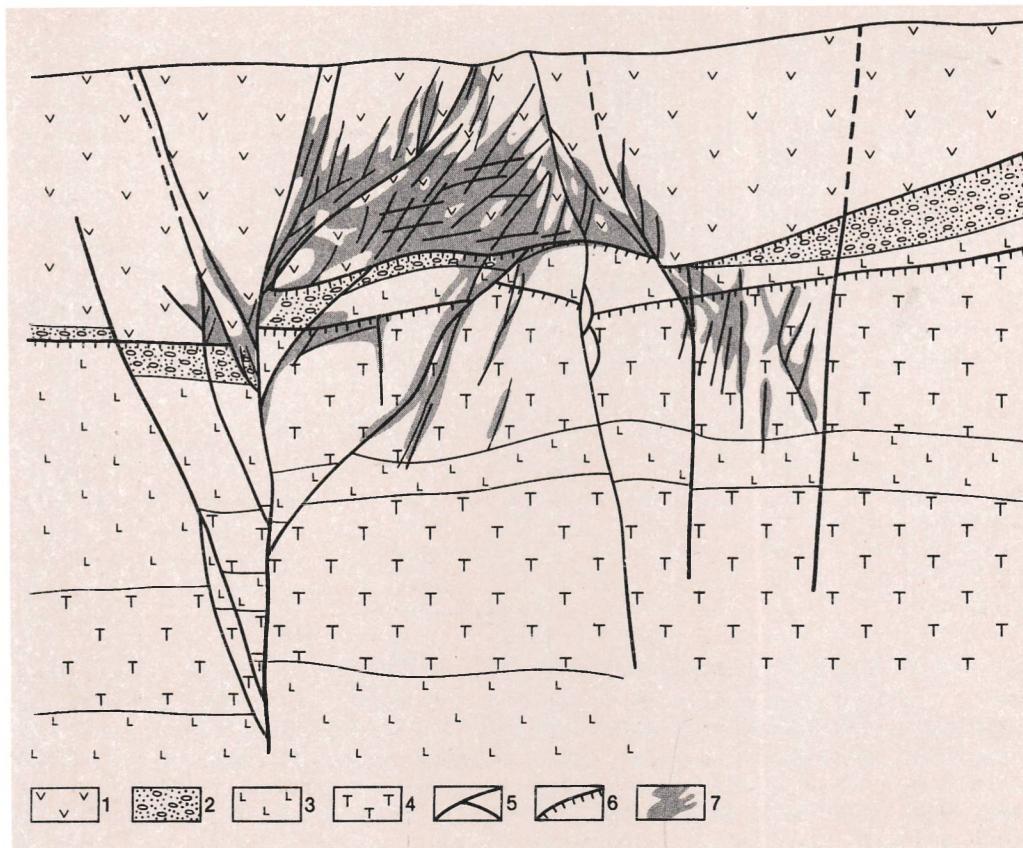
Fig. 144. Geological section across the deposit of a uraninite-fluorite association. (After N. Laverov et al.) [Uranium and Rare-metal Deposits, 1976]:

1–felsites and eruptive felsite breccias;
2–conglomerates;
3–andesite basalt and andesite basalt breccias;
4–dacites and tuffs;

5–steep faults;
6–intrabed faults;
7–ore bodies

V. Danchev [1977] divides sedimentary uranium deposits into marine and continental. Marine deposits occur in carbonate rocks, carbonaceous-silicic shales and phosphate rocks. Continental deposits are found in peat bogs, lignites and brown coal beds, conglomerates and sandstones.

Deposits in Carbonate Rocks

Commercial uranium deposits in carbonate rocks are rare. A deposit described by V. Kotlyar et al [Deposits of Radioactive and Rare Metals, 1973] is located in Paleogene limestones at the periphery of an intermountain basin. Three zones succeed one another from the shoreline outwards: (1) near-shore clastic sediments with carbonate cement; (2) shallow-water oölitic limestone; and (3) deep-water gypsum-clayey-dolomite rocks. Uranium-bearing beds are concentrated in the second zone. They consist of organogenic limestone impregnated by unidentifiable uranium substance. Uraninite accumulations in association with bitumen, coffinite, pyrite, patronite, and lesser amounts of chalcopyrite, sphalerite, galena, iron selenides, hewettite, and melanovanadite were formed as a result of epigenetic processes.

Deposits in Carbonaceous-silicic Shales

Widespread strata of carbonaceous-silicic or "black" shales contain a great amount
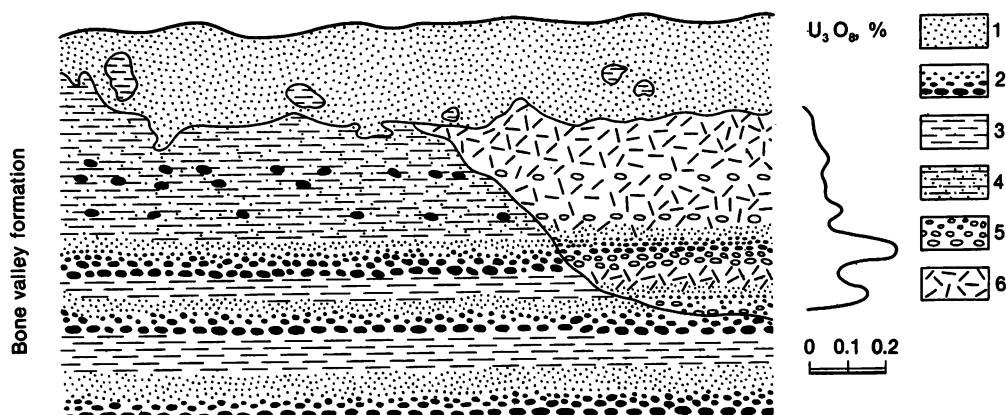
Fig. 145. Section across uranium-bearing phosphorites in the Boun district, Florida. (After Z. Altschuler et al.):

1-3—zone of calcium phosphates:
1—quartz sand;
2—detrital apatite;
3—clays;

4—sandy clays;
5-6—alumophosphate zone:
5—weathered cavernous rock;
6—phosphatized clays

of uranium reaching, according to W. Swanson, 6 million tons. Because of a low metal content (commonly thousandth fractions of a per cent and very rarely 0.01-0.04%), however, these uranium-bearing rocks have never been worked and are considered as the significant resources to be used by the nuclear industry in future. It is only under the action of epigenetic processes of a hypogenic and hypergene nature that the dispersed uranium substance of black shales can be distributed to form minable accumulations of uranium ore. Black shales are distinguished into black shales of geosynclinal seas and those of platform seas. They consist of pelitic and aleuritic material abundant in sapropel and humus organic matter which may be as high as 30% in amount. Black shales are enriched in phosphorus, vanadium, molybdenum, rare earths, and in some places in nickel, cobalt, copper, zinc, lead, and silver. Uranium occurs in ions adsorbed by clay colloids, in urano-organic complexes, and as an isomorphous substitute for calcium in collophane lattice (a colloidal variety of carbonate-apatite).

Deposits in Phosphate Rocks

The deposits of this type are rather widespread, may have significant reserves,

but are very low in uranium content (thousandth fractions of a per cent, rarely up to 0.01-0.05%) and are commercially insufficient. They consist of geosynclinal stratified and platform nodular phosphate rocks. The best known uranium-bearing phosphorite beds occur in the Phosphoria Formation of the Permian age and in the Neogene Bone Valley formation in Florida (USA), and in the Jurassic sediments of North Africa (Tunisia, Algeria, Morocco). Uraniferous rocks are commonly sandstones and more rarely carbonate rocks, marls or clays, in which phosphorite occurs in beds, lenses and nodules (Fig. 145). Phosphorite is usually represented by carbonate-fluo-apatite in which uranium is present as a partial isomorphous substitute for calcium. Phosphatic rocks of this kind are somewhat enriched in vanadium, molybdenum and rare earths.

A variety of the deposits discussed above are accumulations of phosphatized fish bones in clays, in which uranium concentrations, as well as rare earth content, may reach a commercial value.

Deposits in Peat Bogs

Peat bogs are known to be locally enriched in uranium whose content may be as high as
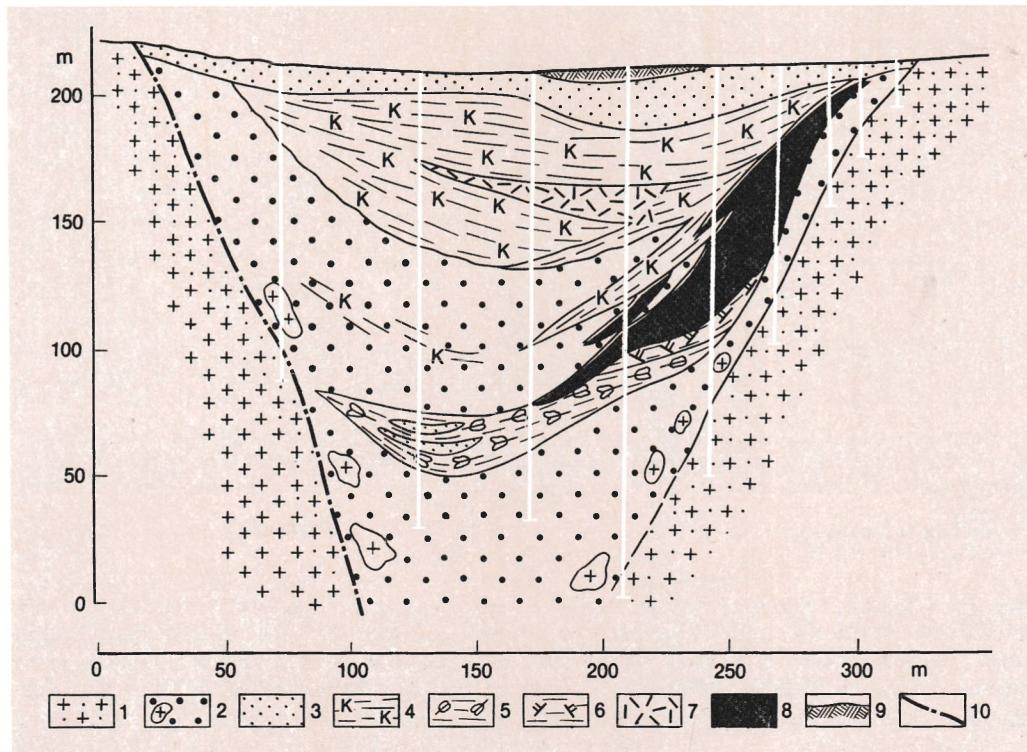
Fig. 146. Geological section across the uranium-coal deposit. (After V. Kotlyar et al.) [Radioactive and Rare-metal Deposits, 1973]:

1—weathered kaolinized granites composing the basement of a trough;
2—coarse diluvium with granite blocks;
3—fine detrital diluvium (gravelstones);
4—kaolinite clays;
5—lacustrine clays with carbonified plant detritus;

6—sapropel clays;
7—tiffites and tuffs;
8—uranium-bearing coal beds;
9—peat;
10—tectonic faults

tenth fractions of a per cent. But usually uraniferous localities are not extensive and hence are not sufficient in reserves. The presence of uranium in peat bogs can be explained by its sorption in the course of peat formation and by the subsequent infiltration of low acidic surface waters leaching uranium from the surrounding rocks and ore deposits.

*Deposits in Brown Coals,
Lignites and Hard Bitumens*

Uraniferous poorly metamorphosed brown coal and lignite beds of late Paleozoic and of a younger age, usually limnic in origin, were formed in intermountain and foremountain basins after a long period of weathering of continental basement rocks,

which facilitated the appearance of easily migrating forms of uranium (Fig. 146). Ore bodies occur in coal beds and in coaly clays, aleurolites and sandstones enriched in carbonaceous matter. They have a form of lenses and pockets confined to permeable roofs or impermeable bottoms of coal beds. Uranium is adsorbed by coal and is present in humates, uraninite and coffinite. A weathering crust of igneous and sedimentary rocks occurring in the sides of coal basins is considered as a source of uranium. The uranium content in coals is usually not more than hundredth fractions of a per cent, but when coal is burnt uranium passes into ash, and its concentration increases manyfold depending on the ash content of the coal. Apart from uranium,
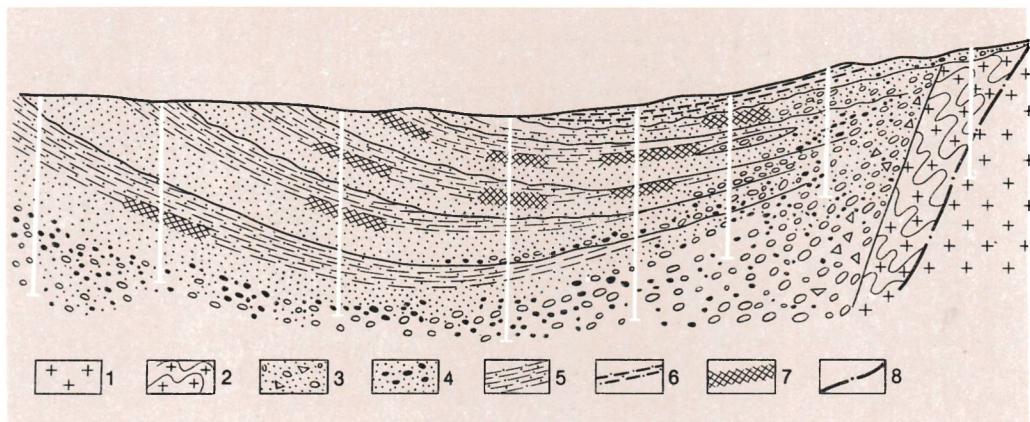
Fig. 147. Schematic geological and lithological section of the uranium deposit in continental detrital rocks. (After V. Kotlyar et al.) [Radioactive and Rare-metal Deposits, 1973]:

1–granitoids;
2–gneisses;
3–breccia-conglomerates;
4–sandstone with gravels;

5–aleurolites;
6–clays;
7–uranium-bearing beds;
8–faults

coal beds contain beryllium and germanium admixtures in the amounts of an economic value. Molybdenum, rhenium, vanadium, arsenic, selenium, nickel, chromium, lead, zinc and other elements may also be present.

Uranium appeared in coal basins at a stage of peat formation, underwent subsequent diagenetic transformation and was enriched as a result of infiltration of uranium containing surface waters and the related surface and deeper intrastratal oxidation.

Accumulations of hard uranium-bearing bitumens which are close in some features to the above formations are believed by some investigators to be of petroleum origin and are considered as products of alteration of vegetable humic substance by the others (V. Kotlyar, 1973). The most prominent deposit of this type is Ambrose Lake, the USA, whose uranium resources were estimated at 120 thous. tons. It occurs in the Triassic sandstones which enclose infiltration uranium deposits of the Colorado Plateau (see below).

Deposits in Detrital Rocks

Uraniferous terrigenous conglomerates, sandstones and clays occur in thick sequences of a diluvial-proluvial facies, which accumulated in piedmont areas. The sequences are often rhythmic in structure with a coarse fragmental material at the base of the rhythms and a fine detritus enriched in humic organic matter and carbonified plant remnants at the top. Uranium ores are confined to the latter (Fig. 147). Ore occurs in sheets and lenses of complicated outlines. Uranium is present in an adsorbed state, in urano-organic compounds, as well as in uraninite and coffinite. Uranium content may be high to be of economic value (tenth fractions of a per cent) depending on the amount of organic matter. Uranium in these deposits was accumulated in the course of sedimentation, in the process of diagenesis, and under the action of interstratal waters infiltration which resulted in its redistribution that made the deposits thus produced look similar to those of the infiltration type which are considered below.

INFILTRATION DEPOSITS

Uranium deposits of the infiltration type originated in an environment of an arid climate primarily under the conditions of intrastratal water infiltration in interbedded sandstones and clays in variegated sequences of continental origin. The most favourable conditions for ore formation existed where water infiltrated along tilted permeable sandstones enclosed in impermeable argilla-
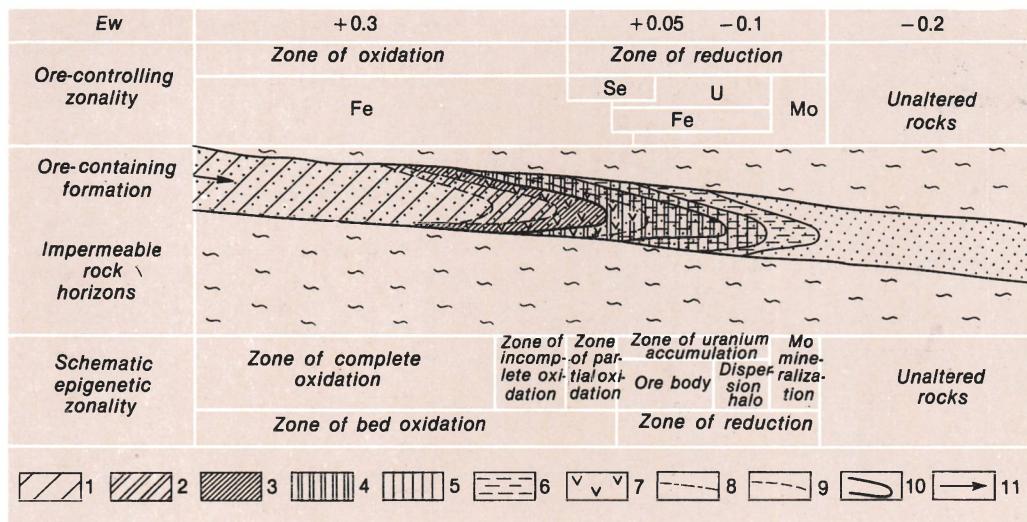
Fig. 148. Diagram of ore-controlling zones in infiltration uranium deposits. (After V. Danchev [1977]):

1–subzone of complete oxidation;
2–subzone of incomplete oxidation;
3–subzone of partial oxidation;
4–subzone of ore body;
5–subzone of uranium halo;
6–subzone of molybdenum mineralization;

7–selenium mineralization;
8–boundary of selenium mineralization;
9–boundary between subzones in a zone of intrastratal oxidation;
10–pinching out of a zone of intrastratal oxidation;
11–direction of intrastratal water flow

ceous rocks. According to V. Danchev infiltration deposits could be formed in sedimentary beds devoid of primary uranium, in those carrying disseminated uranium mineralization, and in the course of redeposition of primary sedimentary ores.

Infiltration deposits consist of three zones: (1) a rear zone of oxidation and leaching; (2) a central zone of secondary ore deposition; and (3) a front zone of unaltered rocks (Fig. 148).

A zone of oxidation contains water enriched in dissolved oxygen which accounts for a positive Eh value. In this zone, uranium passes into a mobile state and is transported by water solutions, and iron oxidizes to a trivalent state and forms iron hydroxides producing a specific brown colour of the rocks.

A zone of reduction and secondary ore deposition is distinguished by a rapid decrease in free oxygen and a jump-like change of a positive Eh value for a negative one. A reducing "geochemical barrier" is thus produced (A. Perelman) causing precipitation of uranium and accessory elements (selenium, molybdenum).

A zone of primary rocks of grey colour is devoid of free oxygen in waters and preserves its original mineral composition.

In view of the fact that intrastratal oxidation occurs under the action of pressure waters in artesian basins, it may extend to a depth of 400-600 m. The resulting ore bodies have a peculiar, often crescent-shaped form (roll bodies) produced by an irregular flow of interstratal waters which is most abundant in the axial parts (Fig. 149). They may reach tens and even hundreds of metres in size and extend in bands for tens of kilometres. The ore consists of pitchblende with some coffinite, seleniferous iron sulfides, native selenium, vanadium minerals, and sulfides of copper, nickel, cobalt and other elements.

Infiltration uranium deposits are of significant economic value and are rather widespread. They are known in Carboniferous-Permian strata in German Federal Republic, Great Britain, Italy, Denmark, the Netherlands, Belgium, Switzerland, Austria, Yugoslavia, Hungary, Romania, and India [*Formation of Uranium Deposits,* 1976]. Well-known deposits in Triassic sandstones
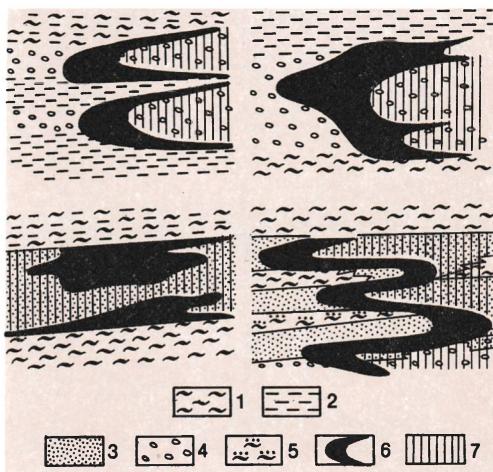
Fig. 149. Typical forms of intrastratal rolls. (After N. Laverov et al.) [Uranium and Rare-metal Deposits, 1976]:

1—aleurolites;
2—clays;
3—sandstones;
4—gravelstones
5—sandy clays;
6—ore body;
7—zone of intrastratal oxidation

of the Colorado Plateau, the USA, and Jurassic and Gretaceous deposits in the USA and Central Europe also belong to this type. Oligocene deposits are known in the USA, France and Egypt, Miocene – in the USA, Japan, Turkey, Pakistan, India, and Spain, and Pliocene – in Japan. The group of infiltration deposits includes very young Pliocene-Quaternary uranium ores in calcretes in Australia.

Metamorphosed uraniferous conglomerates of South Africa and Canada seem to have been originally infiltration deposits.

COLORADO PLATEAU. The plateau is a large block of the North American Platform which was separated from it during the Alpine orogeny of the Cordillera Fold Belt. The basement of the plateau is composed of Precambrian crystalline rocks which are overlain by a slightly deformed cover of Upper Paleozoic, Triassic, Jurassic, Cretaceous and Eocene variegated conglomerates, sandstones and shales with subordinate tuffs and lavas totalling 3 000–4 000 m in thickness. Uranium deposits occur all over the section but most of them are concentrated in Triassic and

Jurassic conglomerates and sandstones. Ore occurs in lenses, tabular bodies and rolls extending for hundreds of metres in length and having a thickness of not more than 5 m (Fig. 150). Primary ore contains uraninite, coffinite, roscoelite, montroseite, some sulfides (pyrite, chalcopyrite, bornite, chalcocite, sphalerite, gersdorffite, smaltite and others), as well as calcite, dolomite, ankerite, barite, fluorite, and kaolinite. A great variety of oxides of uranium, vanadium and other elements are present in the zone of weathering.

The uranium content in the ore ranges between 0.1 and 1%; the ore contains vanadium (1-1.5%), copper, cobalt, nickel, molybdenum, selenium, and arsenic.

YEELIRRIE. This deposit is localized in calcretes in the north-western desert part of Australia. The area is composed of Archean granite gneisses and greenstone rocks covered by residual products of the Meso-Cenozoic weathering crust and Pliocene-Quaternary lacustrine-fluvial deposits. The latter reach 20 m in thickness and consist of alluvial sands, evaporites of dried lakes, and calcretes. Calcretes are the peculiar formations consisting of secondary cavernous dolomite and montmorillonite accumulations produced under the conditions of evaporation of ascending ground waters below the ground surface. In some places calcretes enclose carnotite masses which constitute uranium ore deposits. Uranium and vanadium seem to have been leached by surface waters from the weathering crust, infiltrated into ground waters of the river valleys, and were deposited under the condition of a hot arid climate together with secondary carbonates in the sand and clay fraction of alluvium from the waters rising by capillars towards the ground surface. According to N. Laverov, the principal area of uraniferous calcretes is about 6000 m in extent, 50 m in width, and in average 8 to 10 m in thickness. The U_3O_8 reserves were estimated at 45 thous. tons with the average content of 0.15%.

METAMORPHOGENIC DEPOSITS

No strictly metamorphic types have been identified among the uranium deposits of
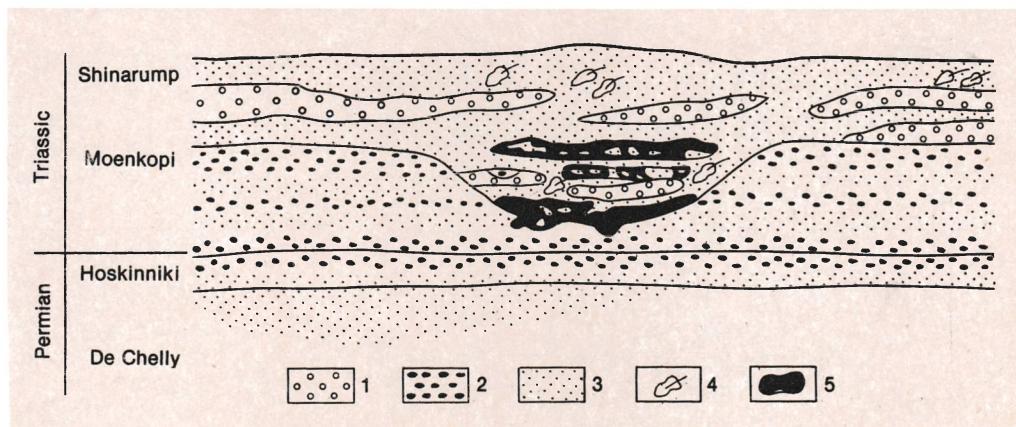
Fig. 150. Shape of ore bodies in the Monument Valley conglomerates and sandstones, Colorado Plateau. (After P. Kerr):

1—conglomerates;
2—argillites;
3—sandstones;

4—fossil plant remnants;
5—uranium ore

metamorphogenic origin, although metamorphosed deposits are rather widespread in Precambrian metamorphic complexes. Worthy of mentioning are skarn-type deposits in Australia, metamorphosed deposits of uraniferous carbonaceous-silicic slates of the Alligator River type in Australia, and old metalliferous conglomerates known in the South African Republic (see Witwatersrand in the chapter "Gold Deposits"), in Canada (Elliot Lake and others), and in Brazil (Jacobina and others).

ALLIGATOR RIVER. A series of uranium deposits (Ranger, Nabarlek, Koongarra, Jabiluka and others) similar in type and origin have been discovered in Northern Territory, Australia. They occur in the Lower Proterozoic Koolpin formation composed of quartz-mica schists, graphitic slates, hornfels, dolomites, and bed-like bodies of basic rocks and tuffs. The deposits consist of a series of stratiform ore bodies complicated by subsequent redistribution of the ore substance controlled by faults and fracture zones (Fig. 151).

The ore occurs in veinlets or is disseminated in quartz-chlorite-sericite schists and graphite slates. It consists of uraninite with subordinate gold, sulfides (galena, pyrite, chalcopyrite, bornite), and hematite. According to N. Laverov and

V. Barsukov, the ore was deposited in four stages. During the first stage (2.2-2 billion years) primary uranium precipitated in geosynclinal carbonaceous sediments and was redistributed during the subsequent diagenesis. During the second stage (2-1.8 billion years) of folding, greenschist metamorphism and hydrothermal activity uranium was redistributed again and probably new portions of it were added from endogenous sources. During the third stage of early platform reactivation (1.6-1.2 billion years) uranium was redistributed again migrating along faults and fracture zones. And final redistribution of uranium resulting in deposition of uraninite devoid of ancient radiogenic lead occurred during the fourth episode of late reactivation (0.7-0.6 billion years).

The uranium reserves in Alligator River were estimated at 300 thous. tons with the U_3O_8 content of 0.1-0.4% in ordinary ore and 15% in high-grade ore.

ELLIOT LAKE. This deposit of uraniferous conglomerates, sometimes referred to as Blind River, is located at the northern shore of Lake Huron in Canada.

Uraniferous conglomerates occur at the base of the Proterozoic metamorphic rocks of the Huronian system which rest with a sharp unconformity on the Archean granite gneiss basement (Fig. 152). The
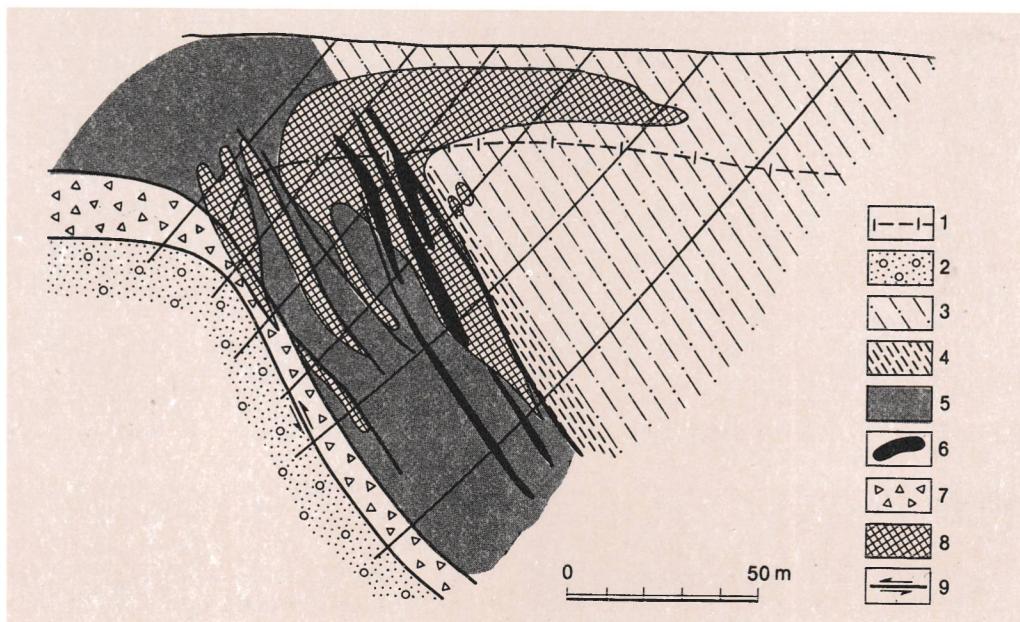
Fig. 151. Section across an ore body in the Koongara deposit, the Alligator River region, Australia. (After G. Ryan):

1—boundary of oxidized zone;
2—Cambodia sandstones;
3—quartz-muscovite-chlorite schists with garnet and pyrite;
4—graphite-quartz-chlorite schists;
5—quartz-chlorite schists;

6—silicic schists;
7—near-fault breccias;
8—ore body;
9—tectonic seams and direction of movements along them
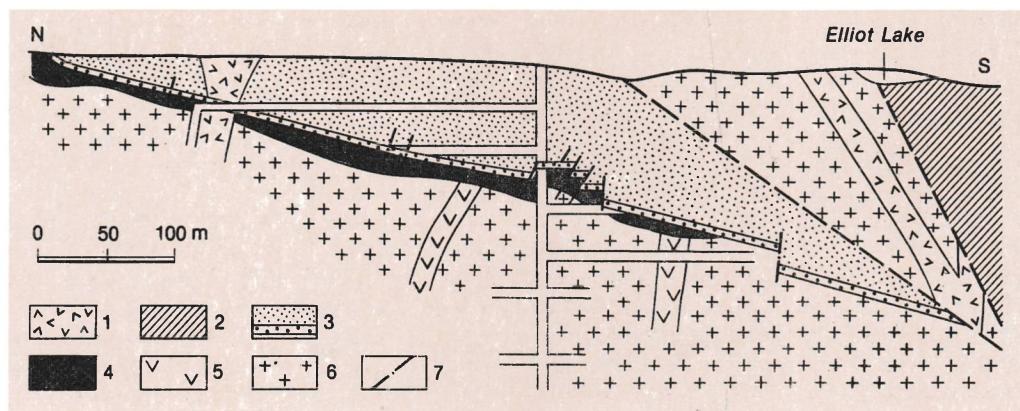
Fig. 152. Geological section of the Elliot Lake deposit, Canada. (After A. Littl et al.):

1—diabase dikes;
2—quartzite and other Huronian rocks lying beneath the Elliot group;
3—pelites, psammites and conglomerates of the Elliot group;

4—underlying uraniferous conglomerates;
5—Archean diabases;
6—Archean granitoids;
7—faults

Huronian system is composed of conglomerates, quartzites, arkoses, argillites and amphibolites totalling a few thousand metres in thickness. The rocks are deformed into a series of gentle folds broken by post-ore faults and cut by diabase dikes. Uraniferous conglomerates occur in beds and lenses. The main bed lies directly on the Archean crystalline rocks extending for 6.5 km and ranging between a few metres and 20 m in thickness. Less important uraniferous beds of smaller size occur upwards in arkoses and quartzites. The conglomerate consists of pebbles and fragments of quartz, more rarely of dark-colour hornfels, about the size of a pigeon egg, cemented by a quartz-sericite-chlorite mass rich in pyrite with hematite, magnetite, monazite, and zircon. The most common uranium mineral is brannerite, and less common is uraninite.

Three stages can be recognized in the ore deposition in Elliot Lake. During the first stage quartz conglomerates with some magnetite, monazite, zircon, and possibly a detrital fraction of uranium minerals were accumulated under paleodelta conditions. During the second stage the conglomerates were enriched in uranium by infiltration of intrastratally circulating ground waters. During the third stage the ore-forming substance was redistributed as a result of greenschist metamorphism.

The Elliot Lake deposit contained 300 thous. tons of uranium ore with the average U_3O_8 content of 0.1%.

36 THORIUM DEPOSITS

Thorium was discovered by J. Berzelius in 1828 in a mineral which was later named thorite when discovered in syenites in Norway. Thorium is used in electric lighting, electric lighting devices, highly refractories, as a catalyst, and in thorium reactors. Current demand for thorium is small, and is about 300 tons per year.

No specific thorium deposits are known. Thorium is recovered as a by-product in the refining of complex rare-element ores. The principal resources of thorium are confined in monazite near-shore placers in Australia, India, Brazil, and Malaysia. In the recent years the annual production of monazite

was 10 to 14 thous. tons which corresponds to 500-700 tons of ThO_2. The price of monazite concentrates at the world market was 200-235 US dollars per ton in 1976. The total reserves of placer monazite in the capitalist and developing countries were estimated at 6-8 mln. tons, i.e. 300-400 thous. tons of ThO_2.

GEOCHEMISTRY AND MINERALOGY

Thorium is the first member of the actinide family having a half-life of $1.39 \cdot 10^{10}$ years. In nature it has virtually only one isotope ^{232}Th. The average thorium content of the earth's crust (clarke) is estimated at $1.5 \cdot 10^{-3}\%$. A perceptible increase in the average Th content from basaltoid to granitoid rocks is noted: $5 \cdot 10^{-7}\%$ in ultrabasic rocks, $5 \cdot 10^{-4}\%$ in basic and intermediate rocks, and $1.8 \cdot 10^{-3}\%$ in acidic rocks. The thorium concentration increases especially markedly in alkaline rocks of both basaltoid and granitoid series reaching $6.5 \cdot 10^{-3}\%$. Accordingly, the geochemical behaviour of thorium in endogenous processes is manifested in its accumulation in granite and especially in alkaline magmas, dispersion in their accessory minerals, and concentration in postmagmatic products such as pegmatites, albitites and hydrothermal derivatives. It is associated with minerals of rare elements, especially tantalum and niobium, rare earths, cerium, yttrium, and uranium. Commonly thorium compounds are deposited prior to uranium ones and are post-magmatic products of a higher temperature. Most of the thorium-bearing minerals are resistant to oxidation and under exogenous conditions are accumulated in placers. About 30 thorium and thorium-bearing minerals are known, the most important of which are:

	%
thorianite ThO_2	(88)
bröggerite $(U, Th)O_2$	(6-15)
thorite $ThSiO_4$	(81.4)
uranothorite $(Th, U)SiO_4$	(50-70)
ferrithorite $(Th, Fe)SiO_4$	(45-65)
thorogummite $(Th, U)[(SiO_4)(OH)]_4$	(45-65)
aeschynite $(Cl, Th)(Nb, Ti)_2O_6$	(20)
priorite $(Y, Th)(Nb, Ti)_2O_6$	(8)
thorium-bearing monazite $(Ce, Th)[(P, Si)O_4]$	(3.5-10 up to 40)

METALLOGENY

The early stage of a geosynclinal cycle with its basaltoid magmatism was not favourable for the emplacement of thorium-bearing deposits. At the intermediate stage, during formation of granite batholiths, thorium-bearing pegmatites appear, which have no practical value. Of somewhat greater importance are albitites and plutonogenic high-temperature hydrothermal deposits associated with alkaline varieties of hypabyssal igneous rocks of the late stage of a geosynclinal cycle.

In the period of tectonic reactivation during a platform cycle of the geological history magmatic thorium-bearing deposits associated with alkaline rocks, and carbonatite thorium-bearing deposits associated with ultrabasic-alkaline rocks developed. Thorium-bearing monazite placers were formed under platform conditions. Both platform-type and geosynclinal alkaline rock associations enclosing thorium-bearing deposits exhibit a tendency to be localized within rigid crustal blocks broken by deep and long-living faults.

Thorium-bearing deposits originated in different periods throughout the geological history of the earth's crust; they are known to occur in Proterozoic, Paleozoic, Mesozoic and Cenozoic rocks. No prominent epochs of thorium deposition can be singled out.

TYPES OF COMMERCIAL DEPOSITS

As mentioned above, no specific thorium deposits have been revealed, and thorium is recovered as a by-product from complex ores of other metals, primarily rare elements and rare earths. Deposits of such ores are known to occur in an endogenous, exogenous and metamorphic environment. Endogenous thorium-bearing deposits include some magmatic deposits (Scandinavian Schield), carbonatites (Mountain Pass, the USA), pegmatites (Canada), albitites (Jos, Nigeria), and hydrothermal deposits (Steenkampskraal, South African Republic; Showderhorn, the USA, and others). The most widespread exogenous deposits are alluvial, proluvial and especially littoral (near-shore) recent and fossil thorium-bearing monazite placers in which the principal resources of the metal are concentrated. Examples of metamorphic deposits are metalliferous conglomerates, e. g. in Witwatersrand, South African Republic, which contain uranothorite, or in Elliot Lake (Canada) which contain thorium-bearing brannerite and monazite.

An example of complex thorium-bearing ores is a deposit described as a representative of a rare earth-base metal association in the chapter "Deposits of Rare Earth Metals and Yttrium".

REFERENCES TO "RADIOACTIVE ELEMENTS" SECTION

Danchev, V. I. Structures and Textures of Uran. Ores in Exog. Deposits. Moscow, Atomizdat, 1977.

Formation of Uranium Deposits. *Proc. of a Symposium on the Formation of Uranium Ore Deposits Organized by the International Atomic Energy Agency,* held in Athens, Greece, 6–10, May, 1974. Intern. Atomic Energy Agency. Vienna, 1974

Geology of Postmagmat. Thorium-rare Met. Deposits. Ed. V. A. Nevskii. Moscow, Atomizdat, 1972.

Kazanskii, V. T., Laverov, N. P. Uranium Deposits. In: *Ore Deposits of the USSR,* 2nd ed. V. 2. Ed. V. I. Smirnov. Moscow, Nedra Publishers, 1978.

Kazanskii, V. I., Laverov, N. P., Tugarinov, A. I. Evolution of Uranium Ore Deposition. Moscow, Atomizdat, 1978.

Nevskii, V. A., Chirkov, I. V. Rare Earth Deposits. In: *Ore Deposits of the USSR,* 2nd ed. V. 3. Ed. V. I. Smirnov. Moscow, Nedra Publishers, 1978.

Radioactive and Rare-metal Deposits. Ed. V. N. Kotlyar. Moscow, Atomizdat, 1973.

Smirnov, V. I. Metallogeny of Uranium. In: *Voprosy Prikladnoi Radiologii* (Problems of Applied Radiology). Moscow, Gosatomizdat, 1963.

Smyslov, A. A. *Uranium and Thorium in the Earth's Crust.* Leningrad, Nedra Publishers, 1974.

Uranium and Rare-metal Deposits. Ed. N. P. Laverov. Moscow, Atomizdat, 1976.

UNIVERSAL REFERENCES

Bateman, A. M. Economic Mineral Deposits. 2nd ed. John Wiley and Sons, New York, 1950.

Bilibin, Yu. A. Metallogenic Provinces and Metallogenic Epochs. Moscow, Gosgeoltekhizdat, 1955.

Course of Ore Deposits. Ed. P. M. Tatarinov and A. E. Karyakina. Leningrad, Nedra, 1975.

Emmons, W. H. The Principles of Economic Geology. USA, 1940.

Fundamental Problems in the Teaching of Magmatic Ore Deposits. Ed. A. G. Betekhtin. Moscow, USSR Ac. Sci., 1955.

Genesis of Endogenous Ore Deposits. Ed. V. I. Smirnov. Moscow, Nedra, 1968.

Kotlyar, V. N. Theoretical Principles of Ore Deposition. Moscow, Nedra, 1970.

Lamey, C. A. Metals and Mineral Deposits. USA, 1966.

Lindgren, W. Mineral Deposits. Translation from English. Ed. B. P. Nekrasov. Moscow, Gorgeolneftizdat, issue 1 and 2, 1934; issue 3, 1935.

Magak'yan, I. G. Mineral Deposits, 2nd ed. Erevan, Armenian Ac. Sci., 1961.

Magnusson, N. H. Malm Geologi. V. 439. Stockholm. 1953.

Niggly, P. Rocks and Mineral Deposits. USA, 1954.

Obruchev, V. A. Mineral Deposits. Moscow, Gorgeolneftizdat, 1934.

Ore Deposits of the USSR. V. 1-3, 2nd ed., revised and suppl. Ed. V. I. Smirnov. Moscow, Nedra, 1978.

Ore Deposits of the United States, 1933-1968. Ed. by D. Ridge. Vol. 1. The American Institute of Mining, Metallurgical and Petroleum Engineers, Inc., New York, 1968.

Park, C. F., MacDiarmid, R. A. Ore Deposits, 3d ed. W. F. Freeman and Co., San Francisco, 1975.

Petraschek, W. E. Lagerstättenlehre. Ein Kurzes Lehrbuch von Bodenschätzen in der Erde. Wein, 1961.

Roethier, P. Les Gisements Metalliferes. V. 1-2, Paris, 1963.

Scheiderhöhn, H. Erzilagerstätten Kurzvorlesunger zur Einführung und zur Wiederholung. Veb Gustav Fischer Verlag, Jena, 1955.

Smirnov, V. I. Geology of Mineral Deposits, 3d ed., revised and suppl. Moscow, Nedra, 1976.

Smirnov, S. S. Mineral Deposits and Metallogeny of the Eastern Territories of the USSR. Moscow, USSR Ac. Sci., 1962.

Svitalskii, N. I. Course of Mineral Deposits. V. 1. Leningrad-Moscow, Gorgeolneftizdat, 1933.

Usov, M. A. A Brief Course of Mineral Deposits. Tomsk, 1933.

Volcanism and Ore Genesis. Ed. by Tansuo Tatsumi. University of Tokyo Press, Tokyo, 1970.

Volfson, F. I., Druzhinin, A. V. Principal Types of Ore Deposits. Moscow, Nedra Publishers, 1975.

LIST OF BASINS AND DEPOSITS

TO THE READER